EXHIBIT E

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Ceramic Dielectrics and Capacitors

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Symbols and Abbreviations

a thermal expansion coefficient
b Curie-Weiss constant
c field coefficient for domain wall velocity
d dissipation factor, $\tan\delta$
e electrode width
f aging rate per decade
g fractional volume
h thickness, skin depth
j $\sqrt{-1}$
k Boltzmann's constant
m dipole moment
n refractive index
p polarizability
q charge on ion or defect
r distance separating ionic sites
s compliance
t time
u, v constants relating K to TCC
w width, length of side
x coefficient in electrical/mechanical loss relation
y exponent in field/thickness relation
z TCC, temperature coefficient of capacitance

A area. In (7.7) constant in non-linear I/V relation.
AC oscillatory current or voltage
B volume
C capacitance
D density
DC continuous current or voltage
E field strength
F oscillator energy

SYMBOLS AND ABBREVIATIONS

G mass
H AC conductivity
I high frequency current
J electrode length
K dielectric constant
L inductance
M molecular weight
N number; N_A, Avogadro's number
P polarization: P_s, spontaneous polarization
Q quality factor, Q = 1/d = 1/tanδ. Narrowness of resonance peak
R resistance
S spontaneous strain
T temperature
TCC temperature coefficient of capacitance
TCK " " " dielectric constant
TCF " " " resonant frequency
U length of perimeter, length of gap
V voltage
W energy of band-gap and of electronic transitions
X coefficient for fringing fields
Y coefficient relating TCK to d
Z impedance

α elimination parameter in PLZT
β polarizability dissipation factor
Γ damping constant
γ breakdown strength per unit area. In (7.7) index in non-linear I/V relation
Δ, δ a small fraction of
ε permittivity, ε" loss factor
ζ lattice spacing
η breakdown safety factor
Θ constant in barrier layer equation
κ Baur's constant
Λ shape factor in mixture relation
λ heat generated in capacitor
μ general property value
ν frequency
ξ screening factor
ρ resistivity
Σ area effect constant
σ function relating internal to external fields
τ leakage constant
φ height of Schottky barrier

χ width of conduction band
Ψ transition probability function
ψ work function
ω angular frequency

Introduction

The objective of this book is to describe the various forms of ceramic dielectrics that have been developed, mainly for the electronics industry, in the last eighty years. The developments are seen against the commercial background which, along with the general evolution of the electronics industry, controlled their emergence.

It is intended to give the ceramist a broad understanding of the electrical side of his products and to give the electronic engineer a better insight into the properties, advantages and limitations of one class of capacitative components.

This book is also a record of the ingenuity of many individuals in making the best of the properties of ceramic materials in one particular branch of industry. It may save the rising generation from "reinventing the wheel" while encouraging its members to do better than their predecessors.

A ceramic is a polycrystalline nonmetallic body made by forming a shape from a powder and heating the shape to impart mechanical strength. This definition excludes single crystals, glasses and cements but might include certain organic materials.

A dielectric is an insulating material that finds use in electrical engineering by virtue of the high impedance it offers to static and low frequency potentials and the relatively loss free impedance it offers to alternating sources. Capacitors, when combined with inductances or resistors can form circuits with controlled time constants. At microwave frequencies a suitably shaped dielectric can form a stable frequency controlling cavity.

Ceramic dielectrics are produced in a wide range of compositions and shapes to cover the applications to which they are better adapted than alternative materials. The technology that has been developed differs considerably from those on which wound polymer film and electrolytic capacitors are based, so that a separate treatment is justifiable. The use of glass dielectrics and of mica has points in common with ceramics: they have similar advantages and limitations when compared with other types. Thus, glass and mica they have been included, even though they lie outside the above definition.

1
Historical

1.1 THE STATUS OF CERAMIC DIELECTRICS

Two advances have led to the present high level of interest in ceramic capacitors. Firstly the discovery of the ferroelectric properties of barium titanate and its high permittivity. Secondly the emergence of a technology for making multilayer ceramic units that match the small size of transistors and integrated circuits and can also survive immersion in a solder bath, so that they are ideally adapted to the economical manufacture of systems on printed circuit boards or hybrid circuits on ceramic substrates.

Impregnated paper and polymer films have low permittiveness so that a reduction in the bulk of capacitors made from them can only come from a reduction in dielectric thickness. Although great progress has been made in this direction, it has not, so far, been able to match the size reduction due to the three orders of magnitude increase in permittivity offered by high-K ceramics, mostly based on barium titanate. Some thin polymer films have, however, the great advantage that breakdowns in dielectrics made from them can be limited to the destruction of a small area of the electrodes and an even smaller area of the dielectric. This 'self-healing' mechanism depends on the deposition of electrodes as very thin (20nm) films, on the chemical composition of the films being such that the breakdown process does not leave a conductive char, and on the ability of organic polymers to absorb mechanical shock without widespread structural damage. There are difficulties in introducing such a self-healing mechanism into ceramic units, principally because the mechanical shock accompanying a breakdown is transmitted through the ceramic with little attenuation and therefore leads to major structural damage and, secondly, because the present methods of manufacture are not readily adaptable to the use of very thin, locally destructible, electrodes.

Electrolytic capacitors also have extremely thin dielectrics combined with a self-healing mechanism that depends on the use of a liquid or semiconducting electrode. This electrode introduces a high series resistance that leads to a high dissipation factor at higher frequencies so that there is little overlap between the applications of ceramic and electrolytic units. Because of the absence of a self-healing mechanism, ceramic units must be designed with larger ratios between breakdown and working voltages than polymer film units. This is a limitation on volumetric efficiency but has the advantage of reducing the probability of small internal discharges.

Ceramic units with even higher capacitance to volume ratios have been made possible by utilising the readiness with which barium titanate can be converted from an insulator to a conductor and vice versa. Ceramic plates can be made in which the bulk of the material is conductive but which have a thin high permittivity insulating layer surrounding each conductive grain or, in simpler structures, have such a layer between the ceramic bulk and the metal electrodes. In this way dielectrics effectively as thin as the thinnest polymer films can be realised, though with limitations with regard to leakage current, loss and working voltage behaviour.

At lower permittivity levels, the ease with which the compositions of ceramics can be varied has led to the development of dielectrics with small and controlled temperature coefficients of capacitance. These ceramics have lower losses and greater stability than high-K materials but can be fabricated into miniature capacitors by the same multilayer techniques. Dielectrics of this type have sufficiently low losses for use as large value transmission capacitors in high frequency power units. Dissipation factors at gigaherz frequencies are in some cases low enough for such ceramics to be used as microwave cavities to control the frequency response of microwave receivers. The working voltage-capacitance ranges covered by the available types of capacitor are shown in figure 1.1.

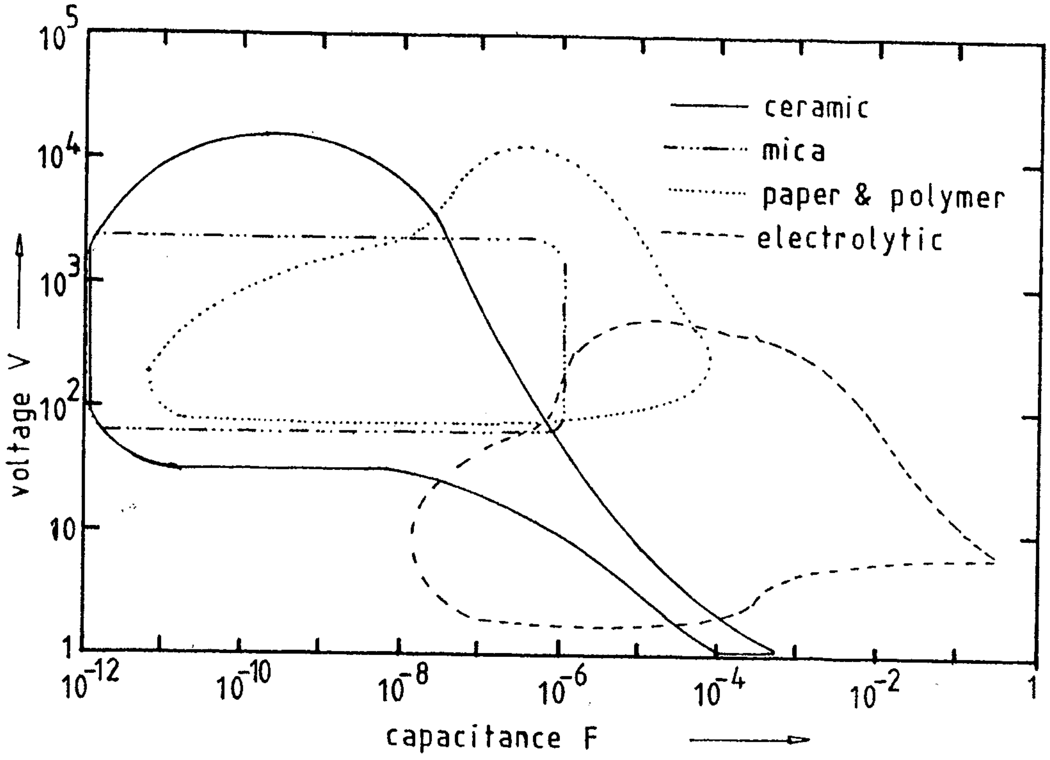


FIGURE 1.1 Working voltage/Capacitance areas for the principal types of capacitor (1)

Hybrid circuits require a substrate to provide a structural base that must also have very stable low loss dielectric properties so that the inevitable stray impedances (sometimes termed parasitics) are reproducible and not in any way deleterious. This has resulted in the production of thin plates of high grade alumina which are adequate for many purposes. At very high frequencies, where the contributions from strays become of major importance, special compositions with low and controlled temperature coefficients of permittivity may be essential. In this case permittivities may also need to be low in order to reduce the level of stray capacitances.

1.2 THE EVOLUTION OF ELECTRONIC CERAMICS

(2) The earliest electrical ceramic used on any scale was probably quartz porcelain (appendix A, table 2). Its main application was as an insulating support for the conductors used in power transmission and telephony. Steatite (appendix A, table 1) was developed in Germany in the

early nineteen hundreds and was both mechanically stronger and capable of manufacture with more precise dimensions than the contemporary porcelain. It also had a lower dielectric loss and was therefore used in electronic systems. In the 1920s steatite was used to make tubular capacitors with values up to 200pF. Its use continued on a large scale up to the 1960s, particularly in the form of valve holders for the high frequency thermionic tubes used in the first stage of television receivers.

Glass (appendix A, table 10) and mica were widely used dielectrics in the early days of electronics. The Leyden jar, a glass pot with its inner surface metallised and its outer surface coated with tin foil, was followed by assemblies of tenth inch thick glass plates, interleaved with zinc electrodes, as the high voltage capacitors required for early radio telegraphy transmitters (3).

The excellent properties of plates cleaved from mica blocks (appendix A, table 4) were recognised in the nineteenth century and capacitors made from stacks of plates interleaved with tinfoil were widely used. In the past fifty years plates of mica with chemically deposited silver electrodes have formed the basis of highly stable units. However, the amount of labour needed for making and assembling mica plates, combined with a diminishing number of mines supplying material of good electrical quality, has increased the cost of mica relative to ceramic units so that the latter are now dominant in many electronic applications.

Interest in aluminous porcelain arose in the fifties with the development of bodies with much higher alumina contents, up to, and sometimes exceeding 99.5%. These materials are stronger than either the porcelains with higher glass contents or steatite, are better insulators and have lower dissipation factors (appendix A, table 2). One major use has been as substrates for hybrid electronic circuits, particularly those involving 'thick film' (or silk-screened) components. These substrates are plates less than 1mm thick with areas of 10 to 100cm^2. Surface finish and overall flatness are closely controlled.

Glass dielectrics were revived in the same period by the manufacture of capacitors from thin glass ribbon formed into stacks of plates with interleaved metal foil electrodes. The resulting units combine high breakdown strength with low circuit noise and great stability. A second development, dating from the sixties onwards, has been the deposition of capacitors onto alumina substrates by silk-screening. The dielectrics usually consist of a high permittivity component mixed with sufficient glass to form a non-porous film, a structure similar to that of porcelain.

Dielectrics with dielectric constants greater than ten (appendix A, table 7) were first produced commercially in the 1930s though the high dielectric constant (approximately 80) of rutile (TiO_2) had been known for many years. In the next decade dielectric constants of several thousand were found to be posible for dielectrics based on barium titanate. These new dielectrics were received with some caution by engineers since the high dielectric constant was accompanied by a high temperature coefficient in the case of titanium dioxide and by both large variations with temperature and higher losses than impregnated paper units in the case of barium titanate. (Appendix B)

The search for a substitute for mica in the USA during the 1939-45 war led to the first monolithic multilayer ceramic capacitor. It was based on a combination of a lead silicate dielectric with silver electrodes and could meet most of the specifications for mica in electronic applications, though the units were not inexpensive.

Work on titanates in the nineteen forties revealed a range of rare earth-titanium dioxide compositions with low loss, dielectric constants up to 700 but rather high temperature coefficients. More widely used dielectrics were derived from magnesium titanate ($MgTiO_3$) which has a positive temperature coefficient of $+100 \times 10^{-6}K^{-1}$ and a constant of 13 (Appendix A, table 7) It can be combined with other oxides with negative temperature coefficients to give dielectrics with coefficients close to zero and low dielectric loss. Several series of these so called NPO dielectrics were derived from titanium dioxide during the forties and fifties and tubular units of up to 1000pF capacitance were used in filter circuits. The use of ceramics was challenged by the development of plastic polystyrene wound film units with temperature coefficients of $-100 \times 10^{-6}K^{-1}$, very low loss and very high insulation resistance. The negative temperature coefficient of polystyrene could be combined conveniently with the positive coefficient of inductance of coils wound on ferrite cores (pot cores) to give filters of sufficient stability for use in telephone systems.

Low loss ceramics with dielectric constants in the 20 to 150 range also found applications, in the form of relatively massive units, in high power high frequency generators.

The high dielectric constant, 1,000 to 10,000, of dielectrics based on barium titanate made it, in the first place, extremely attractive for the manufacture of small single plate (or tubular) capacitors in the 1 to 100nF range. However, its permittivity-temperature characteristic made it necessary to accept a wide toleranc on capacitance value, initially about ±50%, and its dissipation factor of 0.01 to 0.05 made it unsuitable where circuits had to be high in Q. The loss rose above 0.1, and the permittivity either rose by a factor of two or so with high alternating fields or fell by an even larger factor if a high static field were applied (Appendix B). These variabilities and non-linearities were reduced to some extent by modifications to the composition, though usually at the expense of a reduction in permittivity level. On the other hand electronic engineers soon realised that these factors were largely irrelevant to use in the by-pass and decoupling situations which were of frequent occurrence in contemporary television receiver circuits. Most of the early high-K capacitors were tubular since automatic equipment for the production of this shape already existed and the elongated form, similar to that of resistors, was favoured by electronic productio engineers. Flat discs had a small advantage at higher frequencies and gradually replaced tubes as automatic methods for their production became established.

As a result of the introduction of transistors in the fifties and sixties, the working voltages of electronic components fell by two orders of magnitude, while matching the reduction in size from thermionic tubes to semiconductor packages required a reduction in the linear dimensions of at least one order. One response to this change was the 'barrier layer' dielectric. Barium titanate becomes electrically conductive when heated in hydrogen or other reducing atmosphere. Controlled reoxidation creates a thin layer of more or less insulating high-K material on its surface, so that an electroded plate can be made with a conductive core and very thin dielectric layers between the core and the electrodes. To begin with, insulation resistance was poor and the resistive behaviour was that of two back to back rectifiers. However, compositions were found which gave adequate properties for applications of the by-pass class and improvements in technique enabled oxidation to penetrate between the grains of the ceramic and so to increase the effective area of the dielectric. The best results have been based on strontium titanate which can give a working voltage of 10V for a capacitance per unit superficial area of $1 \mu F cm^{-2}$.

Miniaturisation has also been pursued by devising methods of stacking thin layers of ceramic dielectric between electrode systems and the results have been applied over the whole range of available dielectrics.

Ceramics fracture easily under the tensile stresses resulting from flexure and are difficult to fabricate as thin plates which are sufficiently flat not to fracture when a stack of them is subjected to the pressure necessary to form them into a solid block. The problem can be solved by forming the dielectric from a mixture of ceramic powder and a binding agent and applying the electrodes in the form of a fine powder of metal particles. One method is to spray alternate layers of ceramic and metal suspensions. More commonly the ceramic powder and a polymeric organic binder are formed into a continuous tape and a pattern of electrodes, in the form of metal powder, is printed on to this. The tape is then cut up and the pieces stacked and pressed together to form solid blocks. On firing, the binder is burned away and the ceramic and metal sintered to dense blocks. Capacitors with linear dimensions of 2mm or less with capacitances of 1 to 5nF and working voltages of 25 to 50V can be made.

The development of integrated circuits at first appeared to be a threat to the continued use of capacitors as separate units since the smaller values could be replaced by units formed on the surface of the semiconducting chip and the requirements for higher values could mostly be avoided by ingenious circuit design. However the great expansion of electronics in communication and computing has led to an expansion in the use of capacitors in spite of the much smaller number per active element (i.e. transistor structure within an integrated circuit). The monolithic multilayer structure gives a minimum of stray inductance and resistance and so lends itself to use at high frequencies, while the robustness of a ceramic block and its ability to survive high temperature excursions makes it ideal for automated production processes. The two conditions for commercial success are that the component must be both reliable and competitive in cost.

The first multilayer units had platinum or palladium electrodes since these were the only metals that would survive the sintering conditions, 1,300°C in air, necessary for a high resistivity dielectric based on barium titanate. Clearly the replacement of these metals by silver or a base metal would reduce the cost, particularly for capacitance values exceeding 0.1μF. One line of development has been a reduction in the sintering temperature of the dielectric, by the addition of such components as bismuth oxide, so that silver-palladium alloys could be used. More recently complex dielectrics containing lead instead of barium have been produced which can be sintered with silver containing a minimal proportion of palladium. Another method uses a modified barium titanate that yields a high resistivity dielectric when sintered in a slightly reducing atmosphere, so permitting the use of nickel electrodes. A third method substitutes a layer of porous ceramic for the electrodes during sintering and then forms the electrodes by impregnating the capacitor with molten metal. Which of these approaches will eventually turn out to be the most commercially viable is not yet apparent.

2
The Properties of Dielectrics

2.1 UNITS AND DEFINITIONS

S.I. units will be used since they minimise the necessity for numerical coefficients. Conversion to the c.g.s. system is mostly a matter of multiplying by a suitable power of ten. Conversion to inches can generally be carried out with sufficient accuracy by taking 25.4mm to 1 in or 25μm to 0.001 in. For pressure, the approximations: 1 atm=0.1MPa, 1 lb/in^2=7kPa and 1 ton/in^2=15MPa are generally adequate.

The absolute permittivity, ε, will be used where it saves writing $K\varepsilon_o$, where K is the relative permittivity, or dielectric constant, and ε_o is the absolute permittivity of a vacuum, $8.85pFm^{-1}$. Two distinct symbols, ε and K, are used to avoid any confusion. The term high-K denotes a relative permittivity greater than 500, medium-K, one between 15 and 500 and low-K, one below 15.

The capacitance of a parallel plate capacitor, ignoring fringing effects etc. is:-

$$C = \varepsilon A/h \qquad F \qquad ......(2.1)$$

where A is its area and h the separation of the electrodes.

The DC resistance, R_i, of the capacitor, if the dielectric has a resistivity ρ Ωm is :-

$$R_i = \rho h/A \qquad \Omega \qquad ......(2.2)$$

A time constant, τ_i, xan be defined by multiplying (2.1) by (2.2):-

$$\tau_i = CR_i = \rho\varepsilon \qquad s \qquad \ldots\ldots (2.3)$$

τ_i is the time constant for the self-discharge of a capacitor through its own dielectric and is sometimes termed the leakage constant.

The conversion of electrical energy to heat in a capacitor is generally expressed by the power factor, sinδ, where ($\frac{1}{2}\pi$ - δ) is the advance in phase of the current relative to that of an applied alternating voltage. The dissipation factor is defined as tan δ, which will be abbreviated here to 'd'. Since the power factor is the fraction of the voltage-ampere product applied to a capacitor that is lost as heat, it is usually given as a percentage and this usage is commonly extended to the dissipation factor. However the factors for low loss dielectrics are more conveniently given in 10^{-4} units, so that to avoid any confusion, the multipliers will be given in all cases. A dissipation factor of 0.1 is therefore approximately equivalent to a power factor of 10%.

The inverse of the dissipation factor, the Q, is sometimes given. The dielectric loss in a dielectric can also be expressed by putting the permittivity in complex form:-

$$\varepsilon = \varepsilon' - j\varepsilon'' \qquad Fm^{-1} \qquad \ldots\ldots (2.4)$$

ε'' is termed the loss factor. When the electrodes and leads do not contribute to the dissipation factor:-

$$\varepsilon''/\varepsilon' = d_K \qquad \ldots\ldots (2.5)$$

so that $\varepsilon = \varepsilon'(1 - jd_K) \qquad Fm^{-1} \qquad \ldots\ldots (2.6)$

or $K = K'(1 - jd_K) \qquad \ldots\ldots (2.6)$

The losses in a capacitor are often expressed in terms of equivalent resistances, either in series R_s, or parallel, R_p. In the series case, figure 2.1a

$$d_c = \omega CR_s \qquad \ldots\ldots (2.7)$$

where ω is the angular frequency.
In the parallel case, figure 2.1b

$$d_c = 1/\omega CR_p \qquad \ldots\ldots (2.8)$$

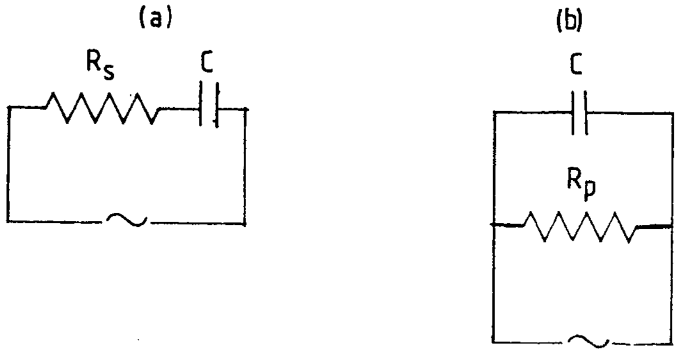


FIGURE 2.1 Series and parallel resistor representations of loss in capacitors.

For the majority of dielectrics R_p is considerably smaller than R_i except near zero frequency. The inverse of R_p, the AC conductance can be related to the AC conductivity, H, of the dielectric through (2.1), (2.5) and (2.8):-

$$H = (1/R_p)(h/A) = \omega\varepsilon'' = \omega\varepsilon' d_K \quad \Omega^{-1}m^{-1} \quad .... \ (2.9)$$

R_s becomes a useful measure of loss in capacitors when the electrodes become a principal contributor, as happens at high frequencies, since R_s then becomes independent of frequency. Since, over the main frequency ranges, the dissipation factor does not vary greatly, both R_p and R_s are approximately inversely proportional to the frequency.

The complete equivalent circuit of a capacitor is given in figure 2.2 (a). For most purposes it can be condensed to that shown in 2.2 (b). In 2.2(a) C_K and R_K represent the capacitance and loss of the dielectric, C_c, and R_c those of the encapsulant due to fringing fields from the dielectric. C_I and R_I represent the capacitance and loss of the interfaces between the electrodes and the dielectric. L_E and R_E represent the inductance and resistance of the electrodes and R_L and C_L those of the leads. C_E and C_L represent capacitances to ground and neighbouring conductors of the electrodes and leads. Th contributions of these components to capacitor behaviour will be considered in succeding sections. It can be see that the components of the simpler equivalent circuit hav complex structures.

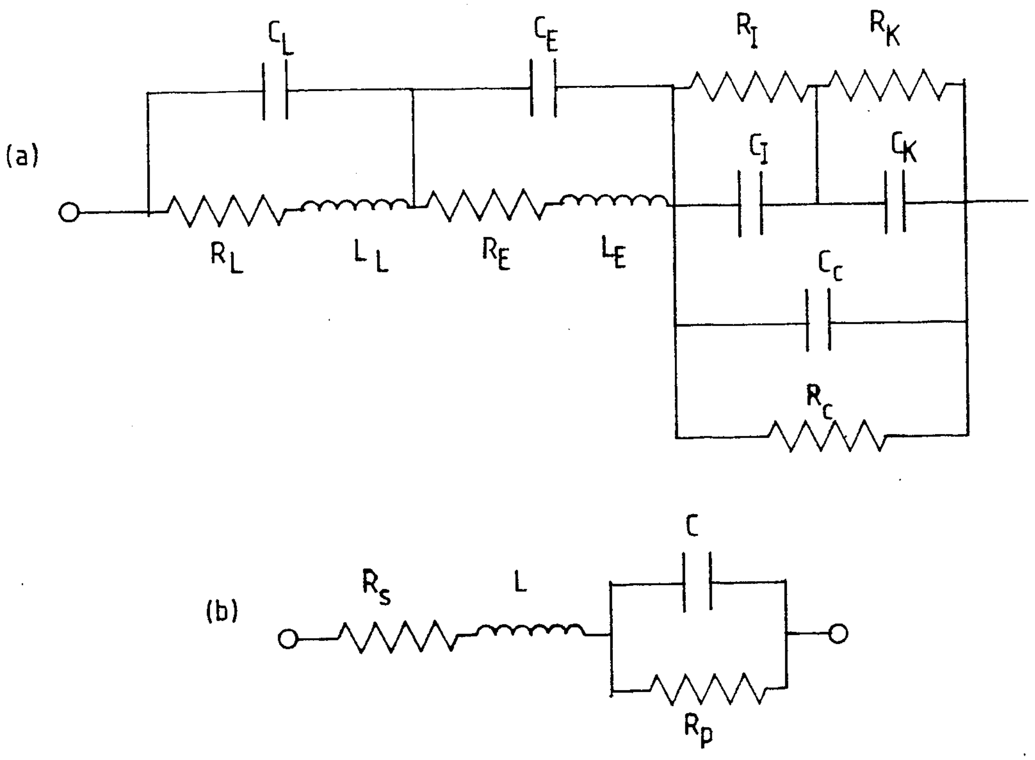


FIGURE 2.2 Detailed equivalent circuits for capacitors.

2.2 POLARIZABILITY

The polarizability, p, relates an induced dipole moment in an atom, ion, molecule etc., to the internal field $\overline{E}_i$ inducing the dipole moment $\overline{m}$, i.e.

$$\overline{m} = p\varepsilon_o\overline{E}_i \qquad \text{Cm} \qquad \ldots\ldots (2.1$$

The polarization, $\overline{P}$, is equal to the product of the numb of polarizable entities per unit volume N ($N=N_AD/M$ where D is the density, M the molecular weight associated wit the polarizable entity and N_A is Avogadro's number) and their moment:-

$$\overline{P} = N\overline{m} \qquad \text{Cm}^{-2} \qquad \ldots\ldots (2.1$$

Since, by defintion,

$$\bar{P} = (K-1)\varepsilon_o\bar{E}_x \qquad Cm^{-2} \qquad ......(2.12)$$

where E_x is the externally applied field it follows from (2.10), (2.11) and (2.12) that :-

$$K-1 = Np(\bar{E}_i/\bar{E}_x) \qquad ......(2.13)$$

The ratio $\bar{E}_i/\bar{E}_x$ depends in a complex manner on the distribution and properties of the surrounding polarizable entities. For a gas at low pressure:-

$$\bar{E}_i/\bar{E}_x = (K+2)/3 \qquad ......(2.14)$$

so that from (2.13) and (2.14):-

$$Np = 3(K-1)/(K+2) \qquad ......(2.15)$$

(2.15) is the Mosotti-Clausius relation that has been extended to isotropic solids for some purposes, but its validity is very limited when applied to the condensed state.

The loss of electrical energy under oscillatory conditions can be expressed by putting the polarizability in complex form:-

$$p = p'(1-j\beta) \qquad m^3 \qquad ......(2.16)$$

where p' is the real part of p and β a constant.
From (2.6), (2.13) and (2.16):-

$$\beta = d_K K'/(K'-1) \qquad ......(2.17)$$

Thus, although the permittivity-polarizability relation in solids is complicated, the dissipation factor and the coefficient β are nearly identical in magnitude.

The following are the principal sources of polarizability:-

p_e, electronic (or optical) due to the movement of the electron charge cloud relative to the nucleus of the atom.

p_i, ionic (or infrared) due to the movement of ions relative to one another and the accompanying displacements of their electron clouds.

p_c, due to localised charge movements in ionic materials and to the rotation of dipoles in polar covalent solids.

p_b, due to interfacial polarization through the presence of a second phase.

p_f, due to the co-operative change in direction of dipoles in the domains of ferroelectric materials. p_i, is the most important contributor to the permittivity in low- and medium-K ceramics. Both p_e and p_i can be related to the inertia of the displaced charges, the electrical restoring force and a damping term proportional to the particle velocity. Each element of polarizability has a characteristic resonant frequency, ω_r, and, with an applied field of lower frequency, ω, the contribution to the polarizability, p_n, is:-

$$p_n = F_n/\{(\omega_r^2-\omega^2)+j\omega\Gamma_n\} \quad Fm^2 \qquad \ldots\ldots(2.18)$$

where F_n and Γ_n are the strengths and clamping constants of the oscillating system (4).
Using (2.16) and equating real and imaginary parts in (2.18) gives:-

$$p_n' = F\{\omega_r^2-\omega^2\}/\{(\omega_r^2-\omega^2)^2+\Gamma_n^2\omega^2\} \quad m^3 \qquad \ldots\ldots(2.19)$$

and $$\beta_n = \Gamma_n\omega/(\omega_r^2-\omega^2) \qquad \ldots\ldots(2.20)$$

At frequencies higher than ω_r, p_n becomes close to zero since the oscillating system cannot follow the applied field; it is said to be clamped. (2.19) and (2.20) are illustrated in figure 2.3.

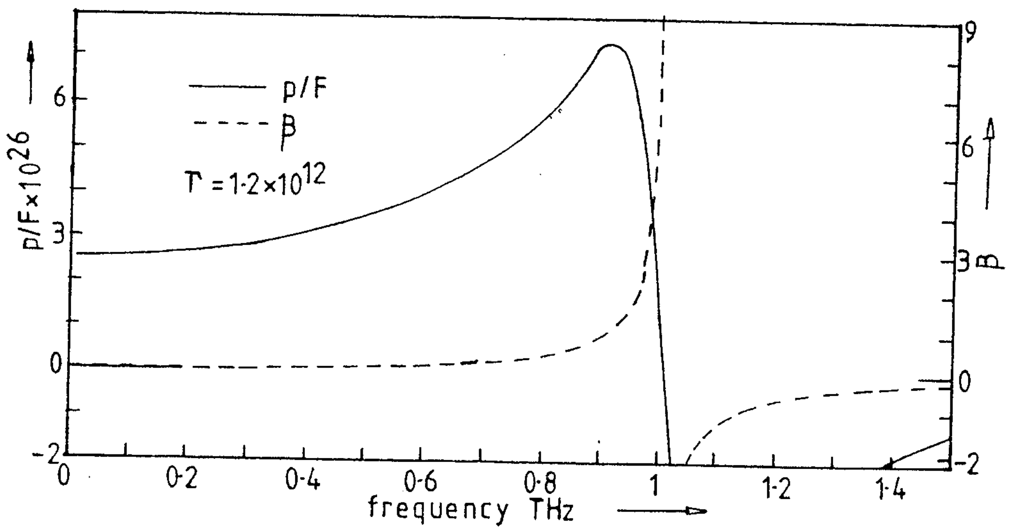


FIGURE 2.3 Polarizability and loss coefficient, β, v frequency from equations (2.19) & (2.20)

p_e gives rise to resonant frequencies at the 10^{15}Hz level, as evident in optical spectra, in which range all the other sources of polarizability are clamped. The optical refractive index, n, is related to the dielectric constant at these frequencies by:-

$$K = n^2 \qquad \text{......(2.21)}$$

The optical effect is constant at low frequencies and accounts for a part of the dielectric constant amounting to 3 in magnesium aluminium spinel to 6 in strontium titanate.

Ionic oscillations have resonances in the 10^{13}Hz region and are responsible for the absorption of infrared radiation. The permittivity increases as the frequency falls through this range reaching a level by about 10^{11}Hz that does not diminish greatly through the succeeding electronic (engineering) region.

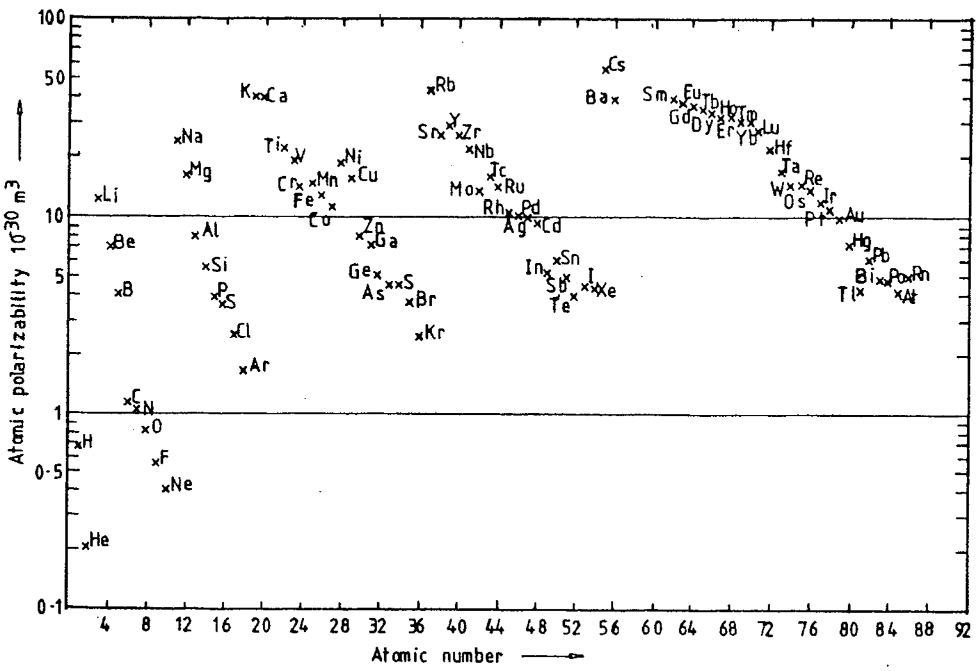
Equation (20) and figure 2.3 indicate that the dielectric loss falls as the frequency diminishes ($d \propto \beta$ according to (2.17))and, since Γ is small for both optical and infrared effects, there is only a very small contribution to the loss from these sources below 10^{11}Hz. However, such losses may be significant in microwave applications (see para. 4.2.5.4).

The contribution of the relative movements of the sublattices of positive and negative ions to the polarizability, p_i, can be calculated from the lattice spacing, ζ, and the compliance, s. For a cubic structure with ions having charges + and - q:-

$$p_i = sq^2/\zeta\varepsilon_o \quad m^3 \qquad \text{...... (2.22)}$$

For sodium chloride $s = 20 \times 10^{-12} m^2/N$, ζ = 200pm so that $p_i = 300 \times 10^{-30} m^3$, which is two orders of magnitude greater than the electronic polarizabilities of the free atoms shown in figure 2.4 (5).

The electronic polarizability of ions can be gauged from the values derived for free atoms as shown in figure 2.4 (6).


Atomic polarizability 10^{-30} m^3
Atomic number
100
50
10
5
1
0·5
0·1
4 8 12 16 20 24 28 32 36 40 44 48 52 56 60 64 68 72 76 80 84 88 92
H
He
Li
Be
B
C
N
O
F
Ne
Na
Mg
Al
Si
P
S
Cl
Ar
K
Ca
Ti
V
Cr
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Y
Zr
Nb
Mo
Tc
Ru
Rh
Pd
Ag
Cd
In
Sn
Sb
Te
I
Xe
Cs
Ba
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Hf
Ta
W
Re
Os
Ir
Pt
Au
Hg
Tl
Pb
Bi
Po
At
Rn

FIGURE 2.4 Atomic polarizability v atomic number.(5)

The polarizability of an ion is close to that of the iso-electronic noble gas, somewhat smaller in the case of a cation and somewhat larger in the case of an anion. Thu sodium and oxygen ions lie below and above neon which has a polarizability of $0.4 \times 10^{-30} m^3$. Barium ions are an orde of magnitude greater than sodium ions in polarizability. The transition element ions do not have noble gas configurations and may be expected to have polarizabilities not very different from that of their atoms.

Limited motion of charge carriers occurs by the mechani known as 'hopping'. A trapped electron may have a finit probability of moving to another site without entering th conduction band. The energetic relationship for hopping can be represented by a double well as in figure 2.5.

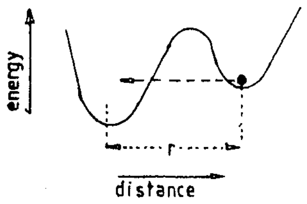

energy
r
distance

FIGURE 2.5 Electron in energy double well.

There is an energy barrier between the two sites which determines the rate at which transitions may occur between them. A field directed along the line joining the sites alters the energy of the entity residing in them and alters the transition rates in the two directions.

When the applied electrical energy is small compared with the thermal energy, kT, it can be shown that the contribution to the polarizability, p_c, for entities with charge q, is given by:-

$$p_c = q^2 r^2 \Psi / 3kT\varepsilon_o \quad m^3 \qquad \ldots\ldots(2.23)$$

where r is the random average of the projection in the field direction of the distance separating the sites and Ψ is a function of the transition probability. $\Psi = 1/4$ when the initial energy levels of the two wells are the same (5),

(2.23) is very similar to the expression for the effect on polarizability of rotating dipoles in solids containing rotatable dipoles.

For a single electron hopping a distance of 300 pm at room temperature, the polarizability, according to (2.23), is 5000×10^{-30} when $\Psi = 0.25$. The effect on the permittivity will depend on the concentration of defects and the extent to which the internal field is raised above the applied field. For a high concentration of defects and/or a high probability of hopping events, there will be a continuous flow of current rather than a limited oscillation between sites. The contribution to the permittivity is small while the resistivity remains at a sufficiently high level for the dielectric to be of practical interest. On the other hand the contribution to the dissipation factor may be of considerable importance (see para 2.3).

Some consideration will be given to interfacial polarization in the next section and to domain effects in the section on high-K dielectrics.

2.3 MIXTURE RULES

2.3.1 Small Concentrations of a Second Phase

Most dielectrics contain small concentrations of other phases. When in the form of a random dispersion of near spherical particles the effect of a second phase on the dielectric constant is given by (7):-

$$K_m = K_2\{1+3g(K_1-K_2)/(2K_2+K_1)\} \qquad \ldots\ldots \ (2.24)$$

where g is the volume concentration (<0.1) of a dispersed phase. K_1, K_2 and K_m are the dielectric constants of the dispersed phase, the matrix and the mixture ($K_2 > K_1$).

Putting the dielectric constants into the complex form, $K=K'(1-jd)$, and equating real parts (taking $g^2=0$):-

$$K'_m = K'_2 \ 1+3g\frac{K_1'^2(1+d_1^2)+K'_1K'_2(1-2d_1d_2+3d_2^2)-2K_2'^2(1+d_2^2)}{(K'_1+2K'_2)^2+(d_1K'_1+2d_2K'_2)^2} \qquad (2.25$$

when d_1, d_2 and $d_1d_2 \to 0$ (2.25) reduces to (2.24).

If the minor phase is conductive with a resistivity ρ_1

$$d_1 = 1/\varepsilon_o\omega\rho_1K_1 \qquad \ldots\ldots(2.26)$$

$$K'_m = K'_2\left[1+3g\frac{1-\varepsilon_o^2\ \omega^2\rho_1^2(K'_2-K'_1)(K'_1+2K'_2)}{1+\varepsilon_o^2\ \omega^2\rho_1^2\ (K'_1+2K'_2)^2}\right] \qquad \ldots\ldots(2.27)$$

provided that terms in d_2^2 and $d_2\rho_1$ are negligible.

When $\omega\rho_1$ is small:-

$$K'_m = K'_2(1+3g) \qquad \ldots\ldots(2.28)$$

That is, well dispersed metallic inclusions will increase the dielectric constant.

When $K'_2 >> K'_1$ (2.27) reduces to:-

$$K'_m = K'_2(1-3g/2) \qquad \ldots\ldots(2.29)$$

This relation can be used to derive the dielectric constan of the fully dense form from that of a slightly porous specimen (7).

Equating the imaginary parts of (2.24)

$$d_m = d_2+\frac{9gK'_1K'_2(d_1-d_2)(1+d_2^2)}{(K'_1+2K'_2)^2+(d_1K'_1+2d_2K'_2)^2} \qquad \ldots\ldots(2.30)$$

(2.30) indicates that the loss will be diminished when $d_2>d_1$, which is the case for low loss inclusions, but is not necessarily the case for inclusions of gas (porosity) since the gas/crystal interface may be lossy through the presence of a high concentration of defects and, at high frequencies, ionisation of the gas may occur. For these reasons $d_2 > d_1$ may not hold in a porous dielectric (see para. 4.1.1.). When the pores are enclosed in glass the gas/solid interface may be relatively inactive. In this case, putting $K_1 = 1, d_1 = 0$ and assuming $d_2^2 << 1$, (2.30) yields:-

$$d_m = d_2\{1 - 9gK_2'/(1+2K_2')^2\} \qquad \ldots\ldots (2.31)$$

Porosity may, therefore, lower the dissipation factor but to a smaller extent when the dielectric constant of the matrix is high.

If the disperse phase is low in resistivity, substitution of (2.26) in (2.30) and the assumption of small d_2 and $d_2\rho_1$ gives:-

$$d_m = d_2 + \frac{9g\varepsilon_o\omega\rho_1K_2'}{1+\varepsilon_o^2\omega^2\rho_1^2(K_1' + 2K_2')^2} \qquad \ldots\ldots (2.32)$$

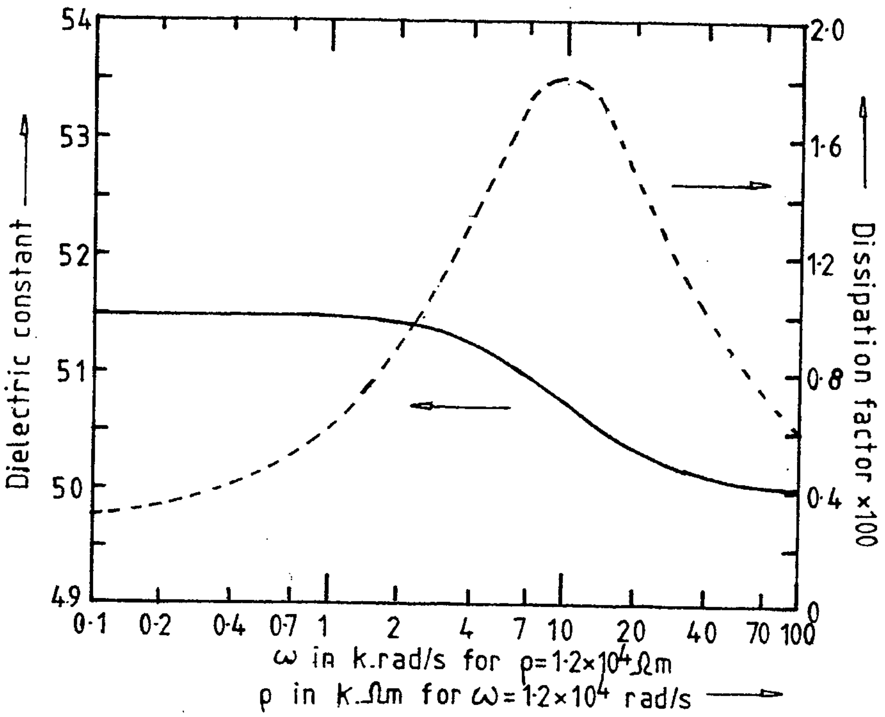
From (2.32) d_m is a maximum when $\omega\rho_1 = 1/\varepsilon_o(K_1'+2K_2')$ (2.33) and the maximum value of d_m is:-

$$d_m(\max) = d_2 + 9gK_2'/2(K_1'+2K_2') \qquad \ldots\ldots (2.34)$$

The relations (2.27) and (2.32) are plotted in figure 2.6, for $K_1 = K_2 = 50$, $g = 0.01$, $d_2 = 0.003$ and $\rho_1 = 1.2\text{x}10^4\Omega\text{m}$.

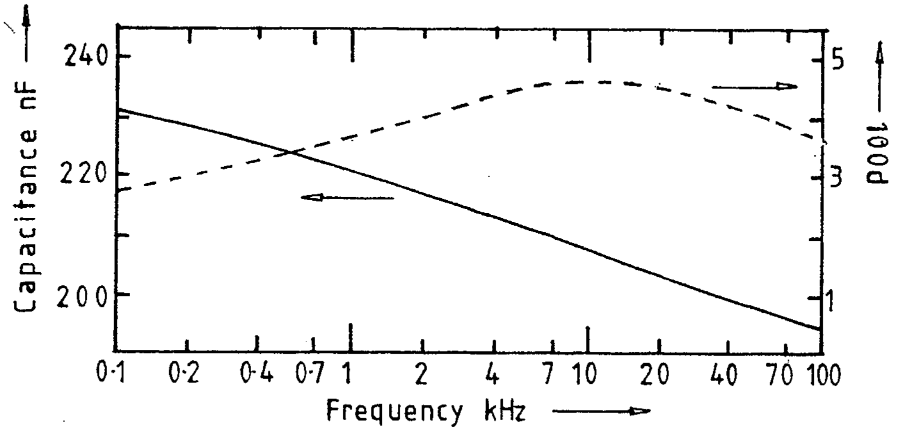
This type of behaviour, exhibited by a mixture of phases, is termed interfacial polarization and is associated with the polarizability p_b referred to in para. 2.2.

Peaks in loss as distinct as that shown in figure 2.6 are seldom seen in ceramic dielectrics because the disperse phases are not usually uniform in resistivity. The matrix and disperse phase usually interact so that the resistivity varies both with particle size and within the particles of the dispersed phase. The dissipation factor frequency relation, shown in figure 2.7, found for a dispersion of manganese oxide in a high-K ceramic (see para. 6.3.2.1.) illustrates what may be seen in certain types of capacitor dielectric (143).



Dielectric constant
Dissipation factor ×100
ω in k.rad/s for ρ=1·2×10⁴Ωm
ρ in kΩm for ω=1·2×10⁴ rad/s

FIGURE 2.6 The effect of a dispersion of conductive particles on dielectric constant and dissipation factor according to (2.27) and (2.32).



Capacitance nF
100d
Frequency kHz

FIGURE 2.7 Capacitance and dissipation factor v frequency for a dielectric containing a conductive phase, as observed. (143)

2.3.2 Large concentrations of a second phase.

Equation (2.24) has been modified to take account of particle shape (8):-

$$K_m = K_2\left[1+\frac{\Lambda g(K_1-K_2)}{\Lambda K_2+(K_1-K_2)(1-g)}\right] \qquad \ldots\ldots(2.35)$$

where Λ is a factor depending on the axial ratio of ellipsoidal particles which are oriented with a principal axis aligned with the applied field. For spheres $\Lambda = 3$. This form shows little improvement on agreement with observation when g is greater than 0.1 though experimental curves can, to some extent, be matched by assuming arbitary values for Λ. The assumed values are unrelated to the observed particle shapes but might relate to the formation of aggregates or chains of particles.

An empirical equation that can often be applied, at least over limited ranges of composition, is the so-called Lichtenecker law:-

$$\log K_m = g_1 \log K_1 + g_2 \log K_2 \;\ldots\ldots \text{ etc.} \quad \ldots\ldots (2.36)$$

where g_1, g_2, etc. are volume fractions of phases with permittivities K_1, K_2, etc. (229).

(2.36) differentiates to give a convenient relation between the temperature coefficient of a mixture and that of its constituents:-

$$(1/K_m)(dK_m/dT) = g_1(1/K_1)(dK_1/dT)+g_2(1/K_2)(dK_2/dT)+ \ldots$$

$$\ldots\ldots \text{ etc.} \qquad \ldots\ldots (2.37)$$

Other relations are:-

$$(K_m-K_2)/3K_m = g(K_1-K_2)/(K_1+2K_m) \qquad \ldots\ldots (2.38)(9)$$

$$(K_1-K_m)/(K_1-K_2) = (1-g)(K_m/K_2)^{1/3} \qquad \ldots\ldots(2.39)(10)$$

Equations (2.24), (2.35), (2.38) and (2.39) give approximate agreement with observation for dilute mixtures. (2.38) has been applied successfully to powders (i.e. $K_2 = 1$) with g exceeding 0.5.

For high concentrations the structural relations between the phases need to be taken into account. There will, for instance, be a marked difference between a dispersion of particles, each isolated from one another by a continuous phase, and a mixture of two phases both of which form continuous networks (11).

2.4 RESISTIVITY

High resistivity is a primary requirement for dielectrics since it underlies one of the main functions of capacitors, the separation of continuous from alternating forms of electrical energy.

Resistivity is controlled, fundamentally, by the energy gap between the conduction and valency bands of the compound concerned, but it may be reduced by the presence of impurities or defects which can release electrons into the conduction band. Donors less than 1eV below the conduction band will be ionised to some extent, at room temperature, by thermal fluctuations and electron will be promoted into the conduction band. Acceptors with similar energies above the valence band may take up electrons and leave 'holes' in the conduction band which serve as p-type current carriers, but these have low mobilities in oxides and only contribute a low level of conductibility.

Conduction may also occur by hopping, that is by thermally assisted transitions between localized sites (1 This is of particular importance where there are transition element impurities since these provide ions of the same element differing by one electron in charge, so that the transfer of charge from one to the other can be accomplished without any overall change in the energy of the system.

The effect of an applied field may not result in the transfer of a carrier from one site to another but simply in the polarization of an electron-lattice site combinati that is an increase in the average separation of the two charges; the result will be a contribution to the permit tivity and the dissipation factor. There is often a correlation between low resistivity and high dissipation factor through both of them being dependent on a high concentration of donors.

Vacant oxygen sites are important donors since in their neutral state they contain two electrons one of which is usually readily ionisable. Oxygen vacancies are formed during sintering and their concentration at room temperature depends on the cooling rate and the oxygen content of the atmosphere. They may be stabilised by the presence of lower valency ions on cation sites, e.g. Ti^{3+} on Ti^{4+} sites, or by cation vacancies.

Impurity ions with charges greater than those of the ions they replace, e.g. La^{3+} on Ba^{2+} or Nb^{5+} on Ti^{4+} sites in barium titanate, also act as donors since the electron necessary to neutralise the excess positive charge is readily promoted into the conduction band.

Electrons will not pass into the conduction band if there are unfilled acceptor sites at lower energy levels. Such acceptors will also immobilise electrons that might otherwise take part in a hopping process. These acceptors may be provided by vacant Ba^{2+} sites in barium titanate or by the presence of impurity ions with lower charges than the cations they displace, e.g. Ga^{3+} or Mn^{3+} on Ti^{4+} sites. Manganese and the iron group transition metals are particularly effective in forming acceptor centres on Ti^{4+} sites when they are present at levels up to 1%. Since they also provide the possibility of conduction by hopping their use in controlling conduction is limited to small concentrations.

High resistivity is best achieved by high purity and a crystal lattice free from defects, but, since defects and impurities are inevitable, the addition of the minimum quantity of a suitable acceptor often gives a marked improvement in practical cases (30).

The permittivity level affects the ionization energy of donors. In a simple electrostatic system the ionisation energy is inversely proportional to the square of the permittivity. Thus the effect of oxygen vacancies in alumina with K=10 is far less than in titania with K=100 or than in barium titanate with K=2000. The highest resistivity ceramics are indeed found among the low-K oxides, particularly silica and alumina,but the resistivities of high-K materials are not as low as this over simplified model might suggest. Their high permittivities result in leakage constants which are similar to those of low-K ceramics.

The probability of a carrier being promoted into the conduction band, or being transferred from one defect to another, is governed by thermal fluctuations that are subject to Boltzmann statistics. One consequence is that the resistivity falls with increasing temperature according to the relation,

$$\rho = \rho_o \exp(W/kT) \quad \Omega m \quad \ldots\ldots \ (2.40)$$

where W is the energy required to promote an electron into the conduction band and k is Boltzmann's constant.

W, for high purity materials, is equal to the band-gap but, when there are appreciable concentrations of impurities and defects, may have a lower value corresponding to the energy gap between an impurity level and the conduction band. As a result wide band-gap materials with lower resistivities due to impurities etc usually have lower temperature coefficients of resistivity than when in the pure state. W then increases at higher temperatures as larger contributions to the concentration of carriers come from deeper energy levels (e.g. figure 2.8).

For most dielectrics the permittivity also falls wit increasing temperature but usually much less markedly tha the resistivity. As a consequence the leakage constant falls with temperature as indicated by (2.3) and (2.40) and this may set an upper temperature limit to the perfor mance of a capacitor.

The resistivity may also change under certain conditions of use, which will be discussed under 'degradation'

Moisture causes a lowering of resistivity if allowed access to most dielectrics, particularly if they contain soluble ionisable constituents. Continuous porosity greatly enhances the effect of moisture. The encapsulation of capacitors, or the circuits containing them, is therefore of great importance in the maintenance of high resistivity. The surface of the dielectric, where it is exposed between the edges of the electrodes, and the lead from the electrodes, are regions which need the most careful protection.

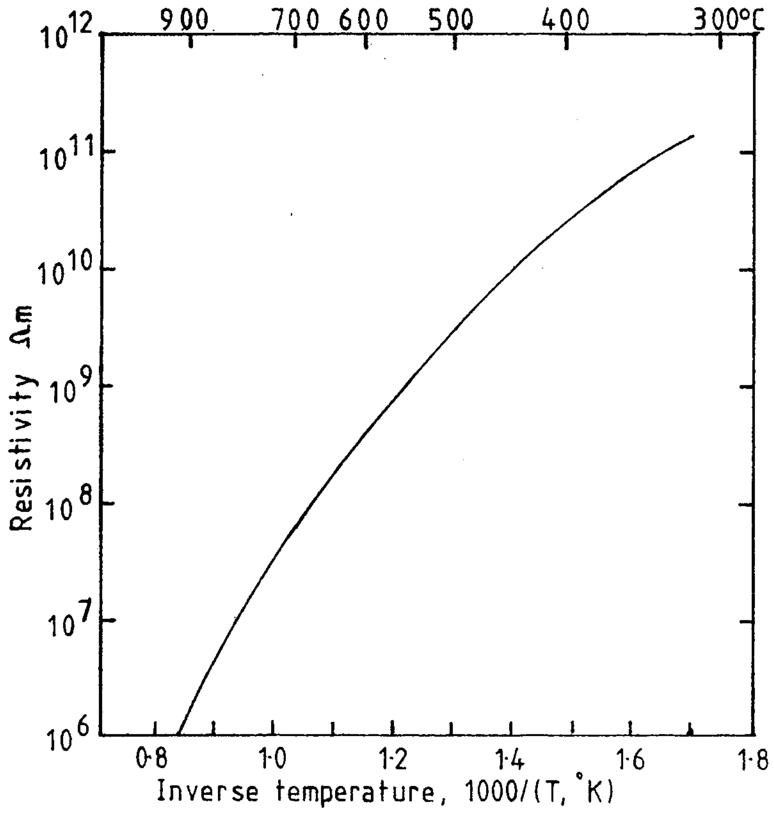

900
700
600
500
400
300°C
10^{12}
10^{11}
10^{10}
10^9
10^8
10^7
10^6
Resistivity Ωm
0·8
1·0
1·2
1·4
1·6
1·8
Inverse temperature, 1000/(T, °K)

FIGURE 2.8 log ρ v 1/T for alumina

2.5 PERMITTIVITY AND POLARIZABILITY

The volume efficiency of a capacitor, C/B, where B is its volume, is, putting B=Ah in (2.2), given by:-

$$C/B = \varepsilon/h^2 \quad Fm^{-3} \qquad \ldots\ldots \ (2.41)$$

It is broadly true that polymer film dielectrics can be made a factor of 10 thinner than ceramics, so that ceramics need to be more than 100 times higher in permittivity if they are to surpass polymers in this aspect of dielectric behaviour. In practice ferroelectric ceramics have an advantage by a factor of 1000 and barrier layer types by one of 10,000 in effective permittivity.

Since the impedance, Z, of a capacitor is inversely proportional to the angular frequency, ω:-

$$Z = 1/\omega C \quad \Omega \qquad \ldots\ldots \ (2.42)$$

the requirement for high permittivities diminishes at higher frequencies. It may even result, above about 1GHz, in a component that is inconveniently small or a substrate giving rise to undesirable coupling between components.

The connection between polarizability and permittivity has been discussed in para 2.2 and no simple relation has emerged. A comparison of the permittivities of different compositions requires an allowance for the number of polarizable entities per unit volume, which can be provided approximately, by dividing the dielectric constant by the density and multiplying by the mean atomic weight.

Table 2.1

Dielectric Constant per average gram-atom

Formula	Dielectric constant K	Density Mgm^{-3} D	Mean atomic weight M_a	KM_a/D
C (diamond)	5.7	2.3	12	30
S	4.1	2.1	32	63
SiO_2 (quartz)	4.5	2.7	20	34
Al_2O_3	10	4.0	20.4	51
MgO	9.7	3.6	20	54
NaCl	5.9	2.2	29.3	80
LiCl	11	2.1	21.3	110
TiO_2	80	4.2	26.4	510
$BaTiO_3$	2000	6	46.6	15000

It appears from this table that a fully covalent material such as diamond, in which the polarizability is expected to be small, has the lowest dielectric constant per atom. Quartz, which has a very low ionicity is close to diamond. Sulphur consists of molecules, S_8, which may contribute to the polarizability and this may account for the higher dielectric constant per atom. Alumina and magnesia with an increased ionicity show increased dielectric constants. Sodium and lithium chloride, which are almost completely ionic show a further increase on a per atom basis. From diamond to sodium chloride the increase in permittivity per atom is less than a factor of 3. The next compound listed, TiO_2(rutile) shows an increase by a factor of 6 over sodium chloride and of 17 over quartz. Barium titanate shows a factor of 30 over rutile.

Materials such as rutile and barium titanate which contain MO_6 groups, where M is an ion of charge 4+ or more, that is isoelectronic with a noble gas, have exceptionally high permittivities. This would appear to be derived from an exceptional ease of displacement of the M ion within the O ion lattice. This culminates, in ferroelectric bodies, in the existence of two or more alternative stable positions for the nucleus of the M atom within the O_6^{2-} octahedron and the possibility of the M ion being switched from one position to another by an external field.

Medium- and high-K ceramics all contain these octahedral O^{2-} structures which may share faces, edges or corners as shown for hexagonal barium titanate, rutile and cubic barium titanate in figures 2.9 a, b and c.

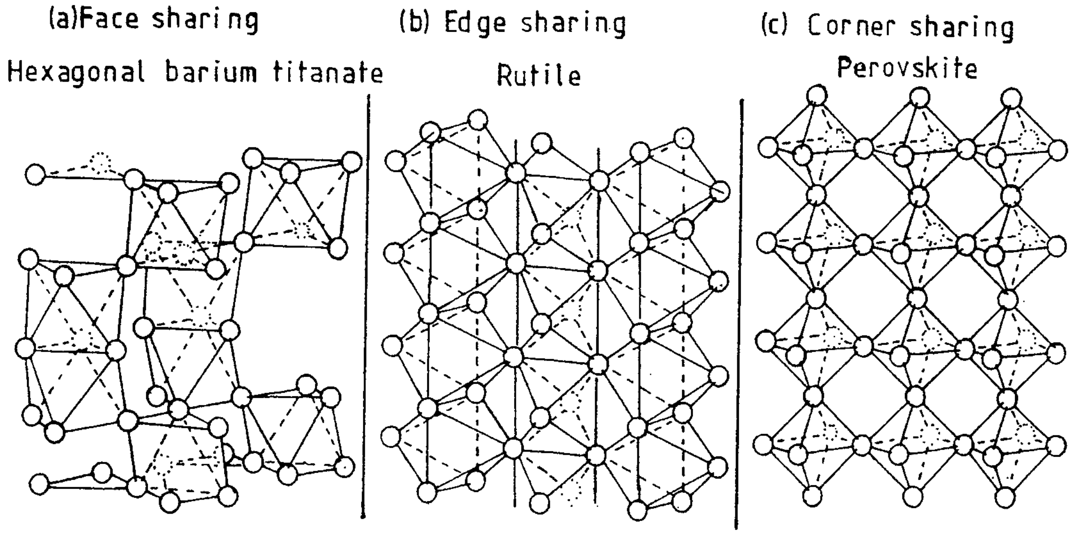


FIGURE 2.9 Face, edge and corner sharing oxygen ion octahedra. (34)

Like barium titanate above 130°C, calcium and strontium titanates have Ti^{4+} ions at the centres of corner sharing octahedra with the alkaline earth ions replacing O^{2-} ions in the close packed O^{2-} array (figure 5.5). They have permittivities of 220 and 440 at room temperature. At room temperature barium titanate contains permanent dipoles which are oriented parallel to one another within regions (domains) which can have dimensions ranging from fractions of a micrometre in ceramics, to centimetres in single crystals. The dipoles are due to spontaneous displacements of the Ti^{4+} ions from the centres of the surrounding octahedra of O^{2-} ions in specific crystallographic directions. The direction of the displacement (the polar axis) can be switched by an applied field i.e. the material is ferroelectric. The very high permittivity has two sources. Firstly the Ti^{4+} and O^{2-} lattices are readily displaced relative to one another in the direction perpendicular to that of the permanent displacement of the Ti^{4+} ions, which leads to a permittivity of about 2000. The permittivity in the direction of the displacement is about 200. The second source arises from the possibility of altering the direction of the Ti^{4+} displacements since this reverses the direction of the spontaneous polarisation (0.27 Cm^{-2}). Thus if 1% of a BT dielectric had its polar axis reversed by a field of $10^5 Vm^{-1}$ the resulting relative permittivity would be about 6000 from this cause alone.

As will be discussed later (para 5.1.1.) ferroelectrics require considerable modification if they are to be used as capacitor dielectrics. Unmodified they have permittivities which vary widely with temperature and with the strengths of the static and alternating fields applied to them. Also their dissipation factors become very high with high alternating fields (see appendix B).

2.6 DIELECTRIC LOSS

A high loss is undesirable in almost all applications It lowers the quality factor of resonant circuits, e.g. in LC filters. It results in the generation of heat and, therefore, in raising the temperature of a capacitor. It is not of great importance in smoothing circuits where the alternating component is to be filtered out of a continuous supply. It could be an advantage in interference suppressors by providing a mechanism for the absorption of high frequency energy, but only if a high dissipation factor (say d=1) could be combined with a high resistivity.

The dissipation factor is generally taken as an indication of the quality of a particular type of capacitor. Thus a value of 0.1 might be acceptable for an aluminium electrolytic unit, 0.02 for a high permittivity (high-K) ceramic and 0.003 for a mica dielectric (figure 1.1). The maximum acceptable value is, therefore, often set at a level that will reject faulty units rather than as a limit determined by an application.

Dielectric loss is due to the conversion of the movement of charges into vibrations of the lattice, i.e. phonons. This can occur from a multiplicity of causes, particularly, as with ceramics, when the microscopic structure is complex.

Both ionic and electronic polarizability involve simultaneous changes in charge distribution round every ion in the lattice. For fields up to the breakdown level and frequencies up to the infrared these changes follow the field with little delay and very little conversion of the electric energy into other forms.

In the case of hopping processes dependent on the presence of defects the situation is somewhat different. Each defect causes an adjustment in the surrounding ions relative to their states when the defect is absent. This adjustment can be represented by a screening charge $-\xi q$ where $+q$ is the charge on the defect and ξ (≤ 1) is a factor representing the incompleteness of the screening due to the restraints imposed by the lattice structure. The movement of the charge to a new site occurs more rapidly than the transfer of the screening charge because the latter involves the interrelated movements of a number of ions (5).

The external field will do work Eqr where r is the projected distance moved by the charge in the field direction, but the energy finally stored in the system will be $Eq\xi r$. Energy is lost through the movement of the screening charge against the applied field. The ratio of energy lost, W_L, to energy stored, W_S, in each hopping transition is:-

$$W_L/W_S = (1-\xi)/\xi \qquad \ldots\ldots(2.43)$$

Although the movement of the screening charge is somewhat delayed with respect to that of the defect charge, the complete transition to another equilibrium state takes a time short compared with the period of the applied field, up to microwave frequencies. The loss is therefore not strongly frequency dependent on this model (5).

The dissipation factors in low- and medium-K materials (Appendix A) can largely be accounted for by a mechanism of the above type. It is a matter of general experience that losses in non-ferroelectric dielectrics can be reduced by purification and the reduction in crystalline imperfections, such as internal strains, so that, for instance, in high quality quartz crystals the dissipation factor may be reduced to a level of 10^{-5} to 10^{-6}.

Porosity results in internal surfaces that are an important source of loss because the surfaces of ceramics contain a high concentration of defects due to the transition from a solid crystal structure to a gas phase. A dense pore free structure is therefore a prerequisite for a low loss dielectric (see para 4.1.1). If the external atmosphere has access to pores they take up moisture which results in an increase in loss, particularly if soluble ions are leached from the solid phase.

Internal surfaces consisting of glass contribute far less to the dissipation factor (see para 4.2.2) since their surfaces are far smoother, and, therefore, effectively far less in specific area than those of ceramics. Since, at low fields, gases have low losses, porosity in glasses, and ceramics containing a high proportion of glass, may reduce the dissipation factor somewhat (see para 2.3.1). At high alternating fields the gas in a pore may be ionised and a plasma formed. This results in a significant increase in loss as well as the possibility of local degradation of the pore surface whether it consists of crystalline or amorphous material.

In ceramics it appears extremely difficult to reduce the dissipation factor below the 10^{-4} level and the residual loss in highly purified fully dense bodies shows very little frequency dependence. It is suggested that the disorder resulting from grain boundaries between randomly oriented crystals and the residual defects in the crystals give rise to tunneling transitions that consist of small adjustments among large numbers of particles in the disordered regions. These transitions, like those associated with the movement of the screening charge, are sufficiently rapid for the associated loss to be independent of frequency up to the 10^{10}Hz level as well as at very low frequencies (13). (An increase in dissipation factor from the 10^{-4} level is observed in medium-K dielectrics above 10^{10}Hz.)

Although the loss due to hopping mechanisms is independent of frequency in the kiloherz region and above, there is an increase in dissipation factor at low frequencies since time is now available for the displacement of defects, such as vacant oxygen sites, as well as electrons. With DC the migration of defects may cause a build up of donor traps near to the electrodes with a corresponding build-up of compensatory space charge, so that an internal field, opposed to the applied field, develops. On removal of the DC field defects and current carriers diffuse back to their equilibrium sites with the development of an external current, if there is a conducting path between the electrodes. This is one of the sources of dielectric absorption and is particularly noticeable in high-K dielectrics in which domain reorientation is an additional factor giving rise to an internal field.

In the case of high-K ceramics the movement of domain walls results in a contribution to the dissipation factor usually in excess of 10^{-3} and this is discussed in para 5.1.2.

An additional source of loss over limited frequency ranges is due to the piezoelectric or electrostrictive effects which are large in many high-K dielectrics. Some of these materials become piezoelectric after the prolonged application of static fields, whilst others vibrate mechanically when both a static and an alternating field are applied together. When the frequency coincides with a dimensional resonance of the capacitor an appreciable fraction of the electrical energy may be transformed into mechanical energy. The order of magnitude of the frequency constant of high-K materials is 1kHzm so that units with dimensions of a few millimetres will have resonances in the 0.1 to 0.5 MHz range with overtones at higher frequencies. Clamping by rigid encapsulants can largely eliminate the effect.

Since the electrostrictive effect is, broadly speaking, proportional to the square of the permittivity, its possible contribution to the loss in lower permittivit bodies is negligible.

2.7 DIELECTRIC ABSORPTION

It is found that when a potential is applied to a capacitor a small current continues to flow and may take a long time to fall to the constant level which correspond to the resistivity of the dielectric. Again, when a capacitor is discharged there will, after a lapse of time, be a small current continuing to flow which exceeds that which would be expected from the charge/time relation of a purely reactive component. If a capacitor is open circuited after discharge a small potential will appear on its electrodes.

This dielectric absorption can be considered due to an extension of the mechanisms causing dielectric loss to very low frequencies. Several processes involving ionic movement may also contribute. One cause is the movement of low mobility defects, such as protons and vacant sites, which are displaced towards one or other of the electrodes by an applied potential and then drift back to an equilibrium distribution when the potential is removed. The return to equilibrium may be hastened by an increase in temperature so that sizeable discharges may occur on heating specimens that have been subjected to potentials for prolonged periods.

The presence of a ferroelectric phase also gives rise to absorption. Domain reversal, which is unaccompanied by any change in lattice dimensions, is permanent until a reverse potential is applied or the dielectric is heated above its Curie point. The movement of the walls between domains at angles other than 180° is accompanied by a change in lattice dimensions and, therefore, by the development of internal stresses. When the field causing the movement is removed the stresses will tend to return the wall to its original position and a discharge current or a rise in potential will result.

Absorption currents may also arise from the depletion of carriers from the Schottky barriers that form under certain conditions at the electrode-dielectric interface and at the interfaces between conductive grains.

Electrodes at which Schottky barriers are formed are said to be 'blocking'. In this case the Fermi level of the metal exceeds that of the dielectric so that any available electrons flow out of the surface of the dielectric into the metal. The source of the electrons is the donor level closest to the conduction band and the depleted region of the dielectric forms the Schottky barrier. The changes in the energy diagram of a dielectric due to the application of blocking electrodes are shown in figure 2.10

If the Fermi level of the metal is less than that of the dielectric the energy levels in the dielectric are bent downwards instead of upwards, since electrons can now flow from the metal into the upper donor level traps, and no barriers are formed.

If there are sufficient acceptors at lower energy levels to balance the donors then, with blocking electrodes, the flow of electrons into the metal will cease when the upper donor level in the bulk of the dielectric coincides with the Fermi level of the metal. The effective work function of the dielectric, ψ_i, is:-

$$\psi_i = \chi + W_1 \qquad ......(2.44)$$

where χ is the width of the conduction band of the dielectric and W_1, the energy level of the donors nearest to the conduction band. The height of the Schottky barrier, ϕ, is given by:-

$$\phi = \psi_m - \chi \qquad ...... (2.45)$$

where ψ_m is the work function of the metal.

If a potential is applied to the capacitor formed by metal plates sandwiching a dielectric with a high insulation resistance, space charge will accumulate in the cathode depletion zone (figure 2.10c). The resulting current external to the system will, initially, be considerably larger than the displacement current due to the increase in space charge in the bulk of the dielectric because of the higher capacitance of the depletion zone

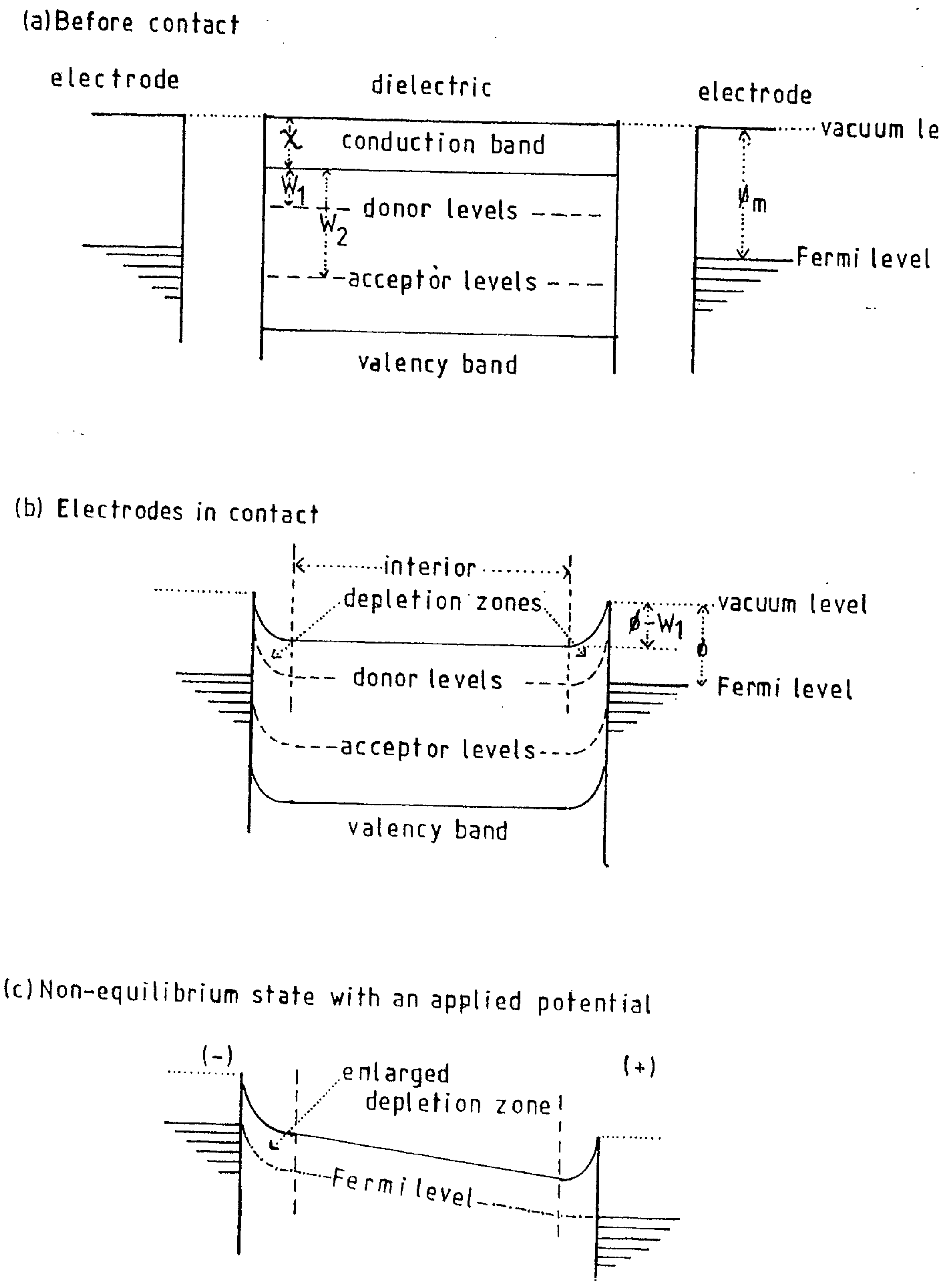

(a)Before contact
electrode
dielectric
electrode
conduction band
χ
W1
W2
donor levels
acceptor levels
valency band
vacuum le
φm
Fermi level
(b) Electrodes in contact
interior
depletion zones
donor levels
acceptor levels
valency band
vacuum level
φ
W1
Fermi level
(c) Non-equilibrium state with an applied potential
(-)
(+)
enlarged
depletion zone
Fermi level

FIGURE 2.10 Energy diagram of dielectric between electrodes. (14)

(which is thin compared with the bulk of the dielectric). There will then be a prolonged period during which the current due to the accumulation of charge in the depletion zone greatly exceeds the equilibrium current that would result solely from the conductivity of the dielectric(14).

One consequence is that measurements of resistivity at room temperature based on apparent equilibrium currents established within minutes, or even hours, of applying a potential through blocking electrodes to a highly insulating material, are usually too low by one or two orders of magnitude. More accurate results are obtainable at temperatures above 200^{o}C: the room temperature value can then be estimated by extrapolation, assuming the logarithm of the resistivity to be inversely proportional to the absolute temperature.

A physically meaningful measurement of absorption is difficult because the currents involved are small and may persist for a long time. Their magnitude is dependent on the applied voltage and the length of time for which it is applied. In practice the effect is gauged by applying a specified potential for a specified time, removing the potential and discharging the capacitor for a defined period, leaving the capacitor open circuit for another defined period and then measuring the potential on its electrodes (figure 2.11). The variables in the test are usually chosen for convenience in measurement rather than for their relevance to practical use. The results of such a test regime for a number of dielectrics is given in table 2.2 (15).

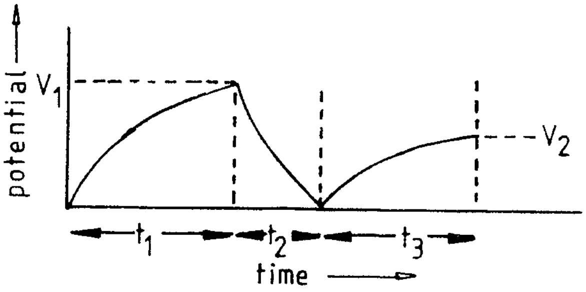


FIGURE 2.11 Test regime for measuring dielectric absorption, V_2/V_1 (15)

Table 2.2

Absorption constants for a range of dielectrics (t_2=10s)

Dielectric	t_1=15, t_3=3 min %	t_1=24, t_3=5 to 10 hr %
Non-polar PTFE	0.01-0.05	0.05-0.10
Non-polar polystyrene	0.02-0.1	0.1-0.2
Polar polyethylene terephthalate	0.2-0.8	1.7-2,5
Paper	0.6-2	30-32
Metallized paper	2-5	39-41
Electrolytic		
Dry aluminium	5-6	15
Dry tantalum	2-5	9-10
Wet tantalum (porous anode)	0.6-2.5	7-8
Mica	2-5	18-20
Ceramic K=150	5	20-22
Ceramic K=900	15	46-47

A test circuit has been devised which gives the voltage/time relation for the t_3 period with t_1=300 and t_2=0.1s and so enables a judgement to be made on the suitability of ceramic units as replacements for polystyrene capacitors in such applications as precision analogue integrator circuits (figure 2.12)(16).

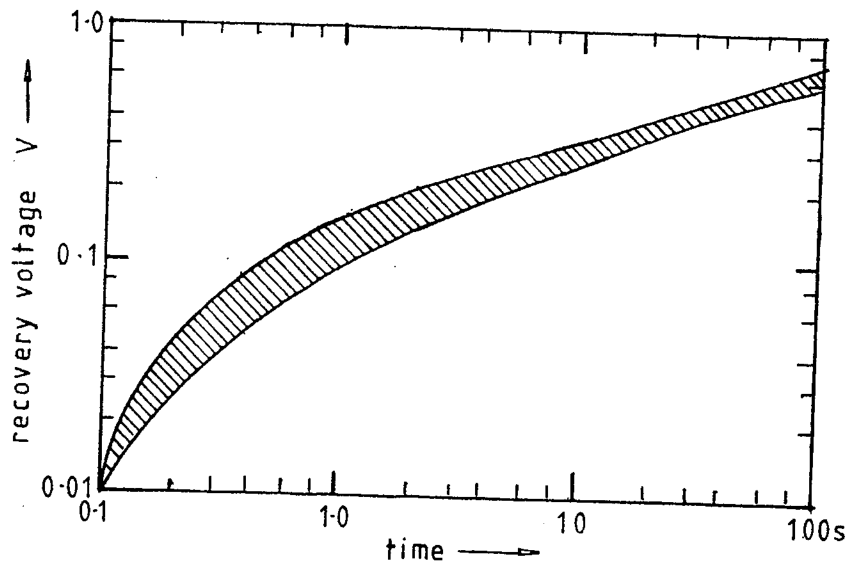


FIGURE 2.12 Limits of recovery voltages for 8 56nF to 10nF ceramic capacitors (16)

2.8 TEMPERATURE COEFFICIENT OF CAPACITANCE

The temperature coefficient of capacitance, (1/C) (dC/dT), (TCC) is of importance where stable values of capacitance are required, as in LC filters. The required level may be zero or a small reproducible value that compensates for a variation in the rest of a circuit. Most high stability applications also require a low dissipation factor.

Differentiation of (2.1) assuming an isotropic dielectric, gives:-

$$(1/C)(\partial C/\partial T) = (1/K)(\partial K/\partial T) + a \quad ....(2.46)$$

where 'a' is the coefficient of linear thermal expansion.

In cases such as mica, where the expansion coefficient in the plane of a plate, 'a_1', differs from that in the perpendicular direction, 'a_2',

$$a = 2a_1 - a_2 \quad ......(2.47)$$

It is clear from (2.45) that the TCC is a material constant that only differs greatly from the temperature coefficient of the dielectric constant, TCK, $(1/K)(\partial K/\partial T)$ when the latter is of similar magnitude to the thermal expansion.

The TCK varies, with notable exceptions, in a regular manner with the permittivity of the dielectric (figure 13). Low permittivity (≃2.5) nonpolar polymers have negative TCKs in the −50 to −400 range (17). Inorganic materials with permittivities less than 10, in which an appreciable fraction of the bonding is ionic, have posiiv coefficients that increase with increasing ionicity.

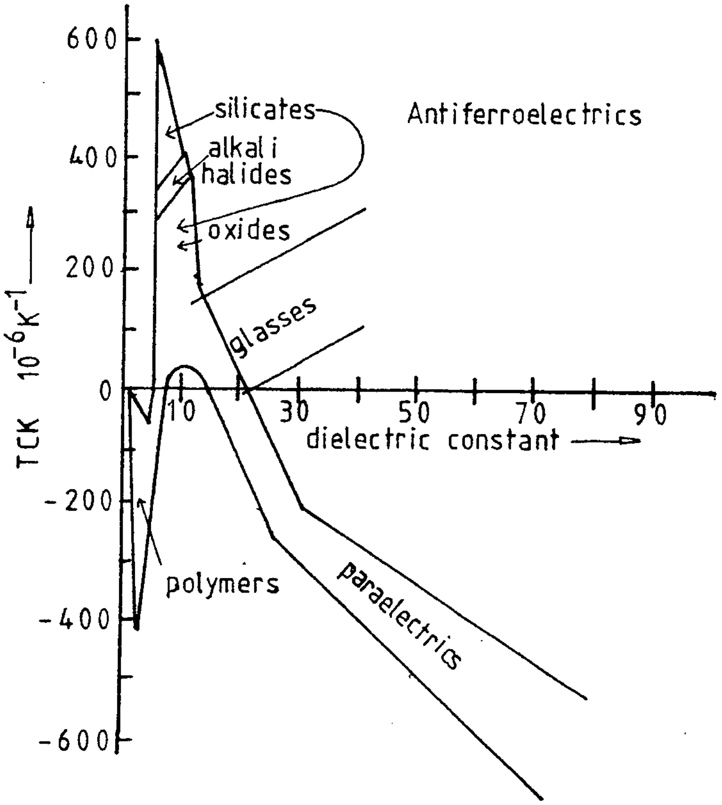
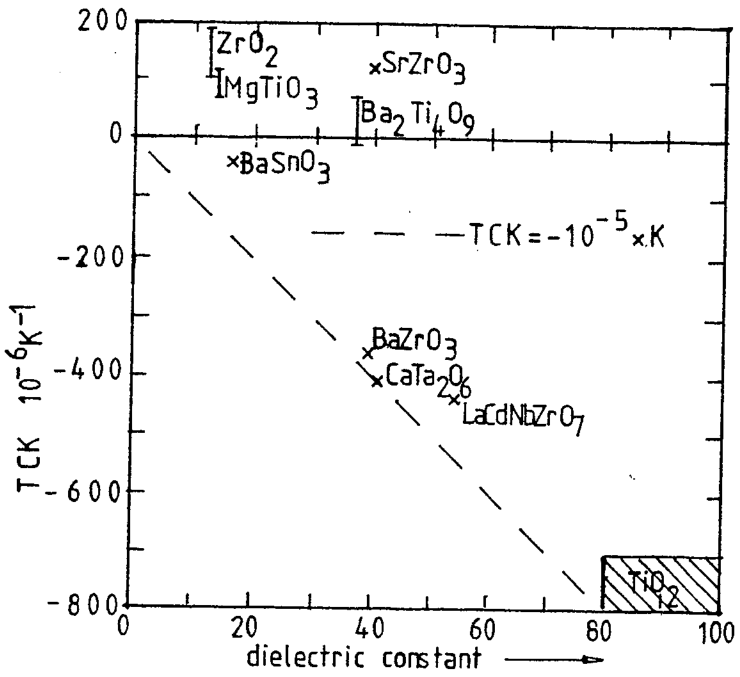

600
400
200
0
-200
-400
-600
TCK 10⁻⁶K⁻¹
silicates
alkali
halides
oxides
glasses
Antiferroelectrics
10
30
50
70
90
dielectric constant
polymers
paraelectrics

FIGURE 2.13 TCK v K for various types of dielectric (17)

For permittivities between 10 and 20 most ceramic materia have positive TCKs but the magnitude falls with increasin permittivity, though this is not the case for glasses which show increases in TCK up to +150ppm/K for permittiv ties up to 30 (Appendix A).

Ceramics with permittivities above 20 mostly have negative coefficients which are within about 30% of the product of their permittivity and their coefficient of linear expansion, which, as the thermal expansion coefficients do not vary greatly (≃10ppm/K) results in an approximate proportionality between TCC and permittivity. The general behaviour is shown in figure 2.13 and that of the higher permittivity ceramics in figure 2.14.



200
0
-200
-400
-600
-800
TCK $10^{-6}K^{-1}$
ZrO_2
$MgTiO_3$
$SrZrO_3$
$Ba_2Ti_4O_9$
$BaSnO_3$
TCK=-10^{-5}×K
$BaZrO_3$
$CaTa_2O_6$
LaCdNbZrO7
TiO_2
0
20
40
60
80
100
dielectric constant

FIGURE 2.14 TCK v K for a range of ceramics.

High-K dielectrics give TCCs which are high and which vary considerably with temperature so that specifications are generally in the form of a tolerance range of ±5 to ±50% of permittivity for a specified temperature range (Appendix B).

The TCK of paraelectric materials has two types of source. The first is due to defects, such as impurity ions, and the second to changes in lattice dimensions and polarizability with temperature.

The contribution of hopping processes and interfacial polarization to the permittivity increases with temperature through the increased thermal energy available to overcome local energy barriers. The temperature coefficient of permittivity from this source is therefore positive. In the case of interfacial polarization an increase in dielec- tric constant with falling resistivity (which could be caused by an increase in temperature) can be seen in figure 2.6. The Boltzmann equation (2.40) gives the temperature dependence in the case of properties dependent on thermal energy to overcome barriers. On differentiation it yield

$$d\rho/dT = -\rho(W/kT^2) \qquad \ldots\ldots(2.48)$$

i.e. the fall in a parameter, such as resistivity, with temperature is proportional to the magnitude of the parameter. Since the loss bears an inverse relation to the resistivity, these considerations make it plausible that there should be a simple relationship between TCK and dissipation factor when the hopping of charge carriers is a major contribution to the loss.

Approaches based on theories of dielectric loss have derived the relation (18, 19):-

$$(1/K)(dK/dT) = (Y/T)d_h \qquad \ldots\ldots (2.49)$$

where Y is a constant about 15 $(^oK)^{-1}$ in value, T the absolute temperature and d_h is the contribution to the dissipation factor from hopping processes. (2.49) describes, approximately, the observed behaviour near room temperature of dielectrics with dissipation factors exceeding 0.005 due to the inclusion of donor dopants. There is a consistent increase, in the positive sense, of the TCC of capacitors when the impurity content of the dielectric increases.

In (2.13), assuming a defect free dielectric, E_i/E_x ma be assumed to be a function, $\sigma(K)$, of the dielectric constant, so that:-

$$K-1 = Np_f\sigma(K) \qquad \ldots\ldots (2.50)$$

where p_f signifies the polarizability of the defect free dielectric.

Differentiation of (2.50) with respect to temperature at constant pressure gives:-

$$\frac{\partial K}{\partial T} = p_f\sigma(K)\frac{\partial N}{\partial T} + N\sigma(K)\frac{\partial p_f}{\partial T} + Np_f\sigma'(K)\frac{\partial K}{\partial T} \qquad \ldots\ldots (2.51)$$

Since $(1/N)(\partial N/\partial T) = -3a$, (2.46), (2.49), and (2.51) can be combined to give:-

$$\frac{1}{C}\frac{\partial C}{\partial T} = \frac{K-1}{K} \frac{-3a+(1/p_f)(\partial p_f/\partial T)}{1-(K-1)\sigma'(K)/\sigma(K)} + a + (Y/T)d_h \quad .... \ (2.52)$$

If σ(K) is given the value (K+2)/3 as for a gas, the function of K in (2.52) reduces to (K-1)(K+2)/3K which approximates to K/3 for higher values of K. The approximate proportionality of the TCC to the dielectric constant, with a coefficient near in magnitude to the linear thermal expansion for a wide range of ionic dielectrics, when due allowance is made for losses due to donor impurities, is consistent with (2.52) provided that the temperature coefficient of the polarizability is assumed to be small relative to the thermal expansion (17).

At lower values of K (K<20) the temperature coefficient of polarizability becomes greater than the thermal expansion term so that the TCC becomes positive, reaches a maximum for the almost wholly ionic alkali halides and declines for the more covalent oxides such as alumina and silica. The TCC eventually becomes negative again for covalent polymers with low dielectric constants, as shown in figure 2.13.

In glasses the TCC becomes increasingly positive up to dielectric constants of 30. In this case the larger ions, Bi, Pb, Cd etc, responsible for the higher polarizability are under less restraint from lattice forces than the ions in crystals.

The dielectric constant of the paraelectric phase of a ferroelectric material obeys the Curie-Weiss relation:-

$$K = b/(T-T_o) \quad ...... \ (2.53)$$

so that the temperature coefficient is:-

$$(1/K)(\partial K/\partial T) = -1/(T-T_o) \ ...... \ (2.54)$$

The TCK is therefore high and negative even if T_o is close to absolute zero.

Dielectrics with low or zero TCCs are desirable in a number of applications. They are readily available with dielectric constants around 20 but, if higher dielectric constants are required, use must be made of the few dielectrics that are exceptional to the general rules outlined above. Sphene, modified bismuth titanate and barium tetratitanate and nonatitanate, given in tables 7, 8 and 9 of Appendix A, are such materials. They contain TiO_6 octahedra but are not ferroelectric (if they were, high dissipation factors would most p bably result in their being of little practical use). Sphene and modified bismuth titanate contain permanent dipoles due to displacements of the Ti^{4+} ions from the centres of their octahedra, but the dipoles are not reversible by an external field. In sphene they are displaced in opposite directions in alternate groups (234) i.e. the structure is antipolar.

In general the TCC of a mixture of phases is equal to the sum of the products of the TCC of each phase and its volume fraction((2.37) para. 2.32) so that a combination of calcium titanate with sphene (tables 7 and 8 appendix A) results in a near zero TCC with a dielectric constant of 80.

It can be seen in (2.52) that the last term, containing d_h, makes a positive contribution to the TCC, however, this is of no practical value in adjusting the TCC to a particular level because the majority of applications for stable dielectrics require a low loss. It is a matter of general experience that, when, through some adventitious factor, a prepartion has an abnormally high dissipation factor, the TCC becomes more positive.

2.9 DIMENSIONS AND STRUCTURE

The relationships between dielectric area and thickness and volumetric efficiency are given in (2.1), (2.41) and (2.74). In general the thickness will be chosen sufficient to sustain the applied potential and the area will then be determined by the required capacitance.

The shape of a unit must be such as to enable it to be handled conveniently and to fit in with other components. It must be capable of bearing the necessary leads or other terminations and to survive their manipulation during insertion in a circuit.

In the case of units which are to pass high currents, the design must take account of the dissipation of the heat generated through dielectric loss and electrode resistance. This will normally be achieved by increasing the exposed area to the greatest possible extent and by having massive leads.

Where heat dissipation is not a problem, a component occupying minimum space will generally be roughly cubic in shape. This can be achieved by stacking the dielectric in layers between a suitable system of electrodes as in monolithic multilayer units (see figure 6.1).

One dimension may be fixed by the desirability of a standard separation between leads so that insertion into circuit boards is simplified. Standardised assembly methods are eased if all the components are the same shape and, since the widely used types of resistors are cylindrical, there has been a demand for tubular capacitors with either axial or parallel leads. The tubular shape results in a stronger body when the dielectric is thin.

Convenience in manufacture is also a factor and has led to the large scale production of disc shaped units pressed from powder on tabletting machines. Disc shaped units also have the advantage over tubes that their stray inductance is slightly less.

2.9.1. Fringing Fields

Equation (2.1) assumes that the edges of the electrodes lie on a surface perpendicular to their principal plane and that the flux outside this surface is negligible. This is only accurate when the separation of the electrodes is small compared with the dimensions determining their area, or when the dielectric has a permittivity greatly exceeding that of the material in which the capacitor is immersed and the electrodes extend to the edges of the dielectric as in figure 2.15(a).

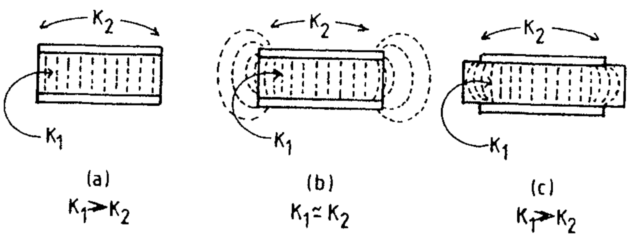


FIGURE 2.15 Fringing fields for various capacitor structures.

In other cases the fringing flux will increase according to the ratio K_2/K_1, where K_1 and K_2 are the dielectric constants of the dielectric and the surrounding medium. For practical purposes the fringing flux reaches a maximum when K_2/K_1 has a value of unity, as in multilayer capacitors. The flux is nearly as large for high- and medium-K dielectrics immersed in a low-K medium when there is a wide margin between the edges of the electrode and the dielectric (figure 2.15(c)). For low-K dielectrics the fringing flux is a complex function of K_2/K_1, the area of dielectric lying outside the electrodes and the dielectic thickness.

The effect of the fringing field can be taken into account as an increase, δA, in the area of electrodes, wher

$$\delta A = XUh \qquad m^2 \qquad \ldots\ldots (2.55)$$

U is the length of the perimeter of the electrodes and X is a factor that covers K_2/K_1 and the structure of the capacitor. X has a maximum value of about 0.3 for the case depicted in figure 2.15 (b) with $K_1=K_2$. In the case shown in 2.15 (a) with $K_1>>K_2$, X=0.

For square electrodes, side w, the ratio of capacitanc due to fringing, C_f, to that due to the area between the electrodes, C_e, is given by:-

$$C_f/C_e = \delta A/w^2 = 4(h/w)X \qquad \ldots\ldots (2.56)$$

since h/w is usually less than 0.1, the fringing field seldom adds more than 10% to the capacitance calculated from (2.1). If, as in the case of figure 2.15(c) with $K_1>>K_2$ or figure 2.15(b) with $K_1=K_2$ the fringing flux is mainly within the same dielectric as the bulk of the unit, its existence does not alter the relations between the permittivity and dissipation factor and the temperature, field or frequency, to any significant extent.

The fringing capacitance is only of importance for low-K dielectrics of small area and relatively large electrode separation. There will then not only be a contribution to the capacitance from the fringing field but also a contribution to the dissipation factor and the TCC dependent on the properties of the surrounding medium.

The effect of the fringing field on the capacitance can usually be ignored but the increased flux density at the edge of the electrode due to fringing results in a considerable enhancement of the local field and can lead to breakdown at high voltages. This aspect is referred to in more detail in paragraphs 2.12.1 and 4.2.5.3.

2.9.2 Coplanar Electrodes

Capacitors are sometimes formed by the deposition of coplanar electrodes on the surface of a dielectric either by silk-screening or vacuum deposition. The resulting units are useful as small capacitances for use at high frequencies in hybrid circuits.

The flux between two coplanar electrodes will have the form shown in figures 2.16(a) and (b).

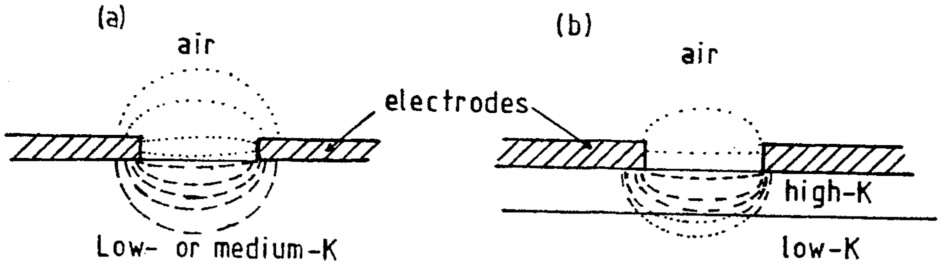


FIGURE 2.16 Flux pattern between coplanar electrodes

In both cases the substrate is likely to be thick compared with the gap width so that the greater part of the flux is, in case (a) within the substrate, and, in case (b), divided between the high-K layer and the substrate. The electrodes will normally be thin compared with the gap width so that the flux passing directly between them will be negligible. The greater part of the capacitance will be due to the fringing field passing through the dielectric. Air may be replaced by a dielectric deposited over the electrodes and gap which will add to the capacitance according to its dielectric constant.

In order to obtain capacitances of sufficient magnitude the electrodes can be formed into the interdigitated pattern shown in figure 2.17.

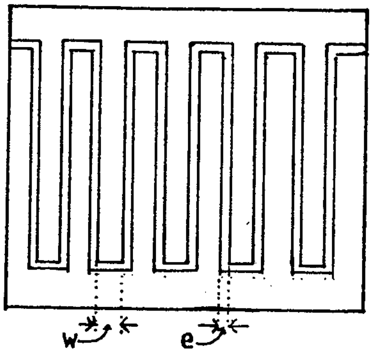


FIGURE 2.17 Interdigitated electrode pattern.

The capacitance of such a unit is proportional to the total length, U, of the gap between the electrodes. As a rough approximation, when the gap and electrode dimensions are minimised, the capacitance is given by:-

$$C = U\varepsilon \quad F \qquad \text{......} \quad (2.57)$$

where ε is the absolute permittivity.

The precise calculation of the capacitance of such units, particularly when they are of the type shown in figure 2.16(b), is complex but close approximations can be achieved by the use of electrostatic theory and computerised calculations (20,21).

The efficient use of available area is secured, in the first place, by reducing the gap, e, between the electrodes and the width, w, of the electrodes. Reducing the spacing between the electrodes increases the capacitance as shown in figure 2.18 for electrodes of effectively infinite width. Reducing the width of the conductors has no appreciable effect while they are greater than 1.5mm wide but there is a steep fall in capacitance when the width is reduced below 0.5mm (figure 2.19). When the electrodes are applied by silk-screening the optimum conductor width usually lies in the 0.25 to 1mm range with gaps down to 0.1mm wide. Much smaller dimensions are possible when the electrodes are vacuum deposited and defined by photolithography as may be necessary when the very small areas available in integrated circuits are to be utilised.

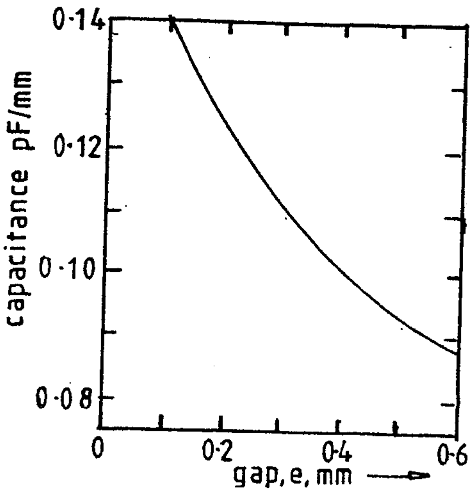


FIGURE 2.18 Capacitance per unit length v gap width (22)

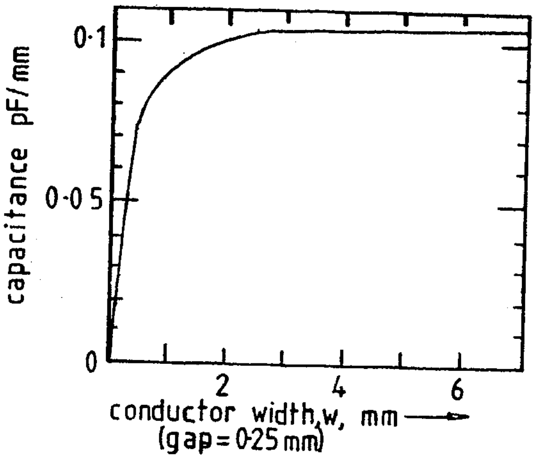


FIGURE 2.19 Capacitance per unit length v electrode width (22)

As the electrode gap is reduced it becomes increasingly important to protect the unit against breakdown by ensuring that the electrode edges are free from protuberances. Protection against gaseous ionisation and, to some extent, the effect of moisture may be obtained by depositing a dielectric over the exposed surface of the electrodes. This can be a glaze in silk-screened devices or amorphous silica in vacuum deposited systems. Such deposits have an appreciable effect on the capacitance. Moisture must be rigidly excluded from such units because of the high dielectric constant of water.

The proximity of conductive surfaces to an interdigitated capacitor has a considerable effect on its capacitance so that the packaging must be taken into consideration when such units are designed.

2.10 STRAY IMPEDANCES

Figure 2.24 can be simplified to the equivalent circuit shown in figure 2.20. C_k is the capacitance due to the dielectric as given by (2), and C_E is a capacitance due to the proximity of other circuit elements and structures. R_E and L_E are the resistance and inductance due to the electrodes and leads.

These strays are partially due to interaction with other components and circuit features, however, the shape and structure of the capacitors accounts for a significant part of them (23). It has, for instance, been estimated that a length of 1cm of 1mm diameter wire located 1cm from another conductor has an inductance of 10nH and a capacitance of 0.18pF which at 300MHz would give rise to reactive impedances of 19Ω and 3kΩ. Moreover the skin effect would result in the resistance of the wire being increased by a factor of 70 at 300MHz compared with DC.

The occurrence of resonance between the effective capacitance, C_f, of a unit and its stray inductance sets an upper frequency limit to the usefulness of a capacitor as a reactive component. The self-resonant frequency , ω_r, ia given by:-

$$\omega_r = (L_e C_f)^{-\frac{1}{2}} \quad \text{rad.s}^{-1} \qquad \ldots\ldots \ (2.58)$$

At resonance the impedance falls to a minimum, R_E, (figure 2.21) largely because of the resistance of the electrodes and the loss becomes very high. At a frequency, ω, below resonance, the stray inductance causes an apparent increase in capacitance to an effective value, C_f:-

$$(C_f - C_o)/C_o = \omega^2/(\omega_r^2 - \omega^2) \qquad \ldots\ldots \ (2.59)$$

where C_o is the capacitance at very low frequencies. The capacitance increases by about 10% when $\omega/\omega_r = 0.3$ according to (2.59).

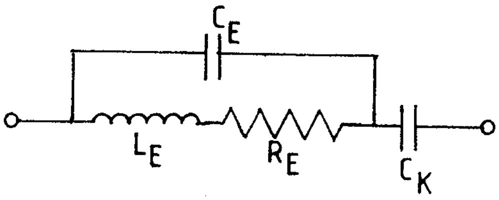


FIGURE 2.20 Equivalent circuit for stray impedances due to the electrodes.

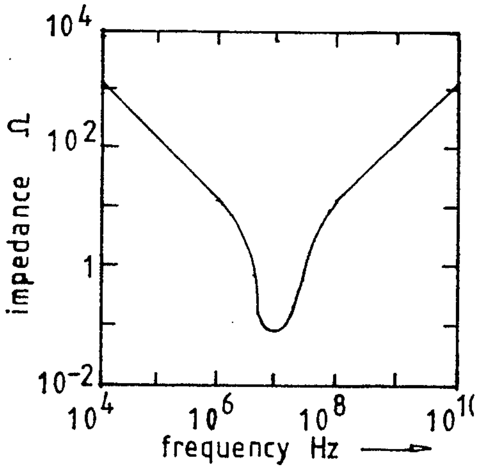


FIGURE 2.21 Impedance v frequency R_E=0.1. L_E=25nH, C_K=10nF, C_E=0

The inductance due to the plates of a capacitor with parallel rectangular electrodes, figure 2.21, has been estimated (24) to be approximately:-

$$L_e = 200J(\ln(2J/w)+\tfrac{1}{2}+w/J)\times10^{-9} \quad H \quad .... (2.60)$$

where w is the width and J the overall length of electrodes resulting in an inductance L_e. This is also the inductance associated with a stack of similar units. The inductance is a minumum when J = w (see para. 6.2). It will be increased by the inductance of the link connecting the capacitor to the rest of the circuit.

(2.58) and (2.60) can be used to compare the self-resonant frequencies, ω_1 and ω_2, of units having the same capacitance and shape but different dielectrics with differing property values indicated by subscripts 1 and 2. Suppose that the units consist of N layers with J=w, then from (2.58) and (2.60):-

$$\omega_1/\omega_2 = (J_2/J_1)^{\frac{1}{2}} \quad ...... (2.61)$$

for equal capacitance:-

$$N_1K_1J_1/h_1 = N_2K_2J_2/h_2 \quad ...... (2.62)$$

For the same shape:-

$$J_1/N_1h_1 = J_2/N_2h_2 \quad ...... (2.63)$$

Combining (2.61), (2.62) and (2.63):-

$$\omega_1/\omega_2 = (h_2/h_1)^{1/2}(K_1/K_2)^{1/4} \quad ...... (2.64)$$

(2.64) indicates that small variations in K and h will not greatly affect the self-resonant frequency. Comparing a high-K ceramic with a polymer film capacitor with h_1=25μm, h_2=1.5μm, K_1=4000, K_2=2.5, we get $\omega_1/\omega_2 \simeq 1.5$. The greater area required for the plates of the lower permittivity material accounts for the lower self-resonant frequency in that case.

The loss at high frequencies is best considered in terms of the equivalent series resistance since it is usually due to the resistance of the electrodes, which may be increased by the skin effect.

The effective resistance of a plate in a structure su as that shown in figure 2.22 has been estimated to be (24

$$R_s = \rho_s(1/3w)(3J_e+J_o) \quad \Omega \qquad \ldots\ldots (2.65$$

where ρ_s is the resistivity per square, w the width of th electrodes, J_o, the length of the overlapping part and J_e the length of the non-overlapping part of an electrode.

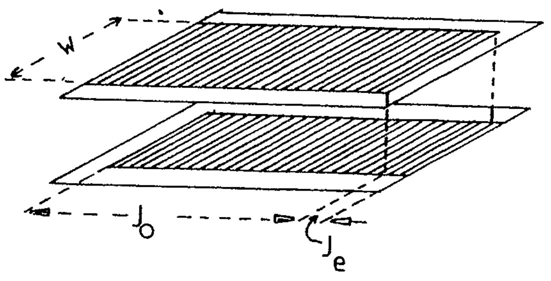


FIGURE 2.22 Overlapping electrodes.

At frequencies and dielectric thicknesses where the value of ρ_s is dominated by the skin effect:-

$$\rho_s \simeq 2\text{x}10^{-3}(\nu\rho_e)^{\frac{1}{2}} \quad \Omega \qquad \ldots\ldots (2.66$$

where ρ_e is the resistivity of the electrode metal in Ωm ν is the frequency and the relative permeability of the electrode is assumed to be unity.

Combining (2.65) and (2.66) and assuming a two electrode unit:-

$$R_s = 4(\nu\rho_e)^{\frac{1}{2}}(1/3w)(3J_e+J_o)\text{x}10^{-3} \quad \Omega \qquad \ldots\ldots (2.67)$$

in agreement with (2.67) it is found that the equivalent series resistance of units with relatively thick silver electrodes increases as $\nu^{\frac{1}{2}}$ above about 200MHz (23). R_s shows a continuous increase through the resonant region without the peak shown by the dissipation factor.

The electrode resistance of a multilayer stack containing N layers has been estimated (24) to be:-

$$R_s = (2/3)(2-1/N)(\rho_s/w)(3J_e+J_o) \qquad \ldots\ldots (2.68)$$

At frequencies for which the skin effect is negligible $\rho_s=\rho/h_e$ where h_e is the electrode thickness. Making the approximations $(2-1/N)=2$ and $(1+3J_e/J_o)=1.5$ (2.68) becomes:-

$$R_s = 2\rho_e J_o/wh_e \qquad \text{......} \quad (2.69)$$

The part of the dissipation factor, $2\pi\nu CR_s$. attributable to the electrode resistance is, from (2.69):-

$$d_s = 4\pi\nu C(\rho_e/h_e)(J_o/w) \qquad \text{......} \quad (2.70)$$

A multilayer ceramic capacitor might have an electrode thickness of 3μm with resistivity 10^{-7}Ωm (for Pd) so that, at 1 MHz and taking $J_o/w=1$, the maximum capacitance at which the dissipation factor could be below 0.02 would be 48nF.

For a polymer film capacitor to be self-healing h_e cannot exceed 0.02μm, so that if $\rho=2.5\text{x}10^{-8}$Ωm (for Al) the maximum capacitance under the same conditions would be 1.3nF.

It is evident that electrodes may be a source of dielectric loss when high value units are used at high frequencies.

2.11 ELECTRODES

The effect of the resistivity and thickness of the electrodes has been considered in the preceding paragraph. The loss can be kept down at high frequencies by increasing the electrode thickness but above 100MHz the surface resistance is controlled by the skin effect so that the only means of improvement is to use a low resistivity metal.

The electrode may contribute to the parasitic capacitance, C_I, (figure 2.23) if it does not form a close joint with the dielectric. If the electrodes are separated from the dielectric by a layer of thickness h_g and permittivity K_g the capacitance of the unit will be:-

$$C_I = AKK_g\varepsilon_o(hk_g+2h_gK) \quad \text{F} \qquad \text{......} \quad (2.71)$$

The ratio of the capacitance, C_K, of a unit without gaps to one with is:-

$$C_K/C_I = 1+2(h_g/h)(K/K_g) \quad .... \quad (2.72)$$

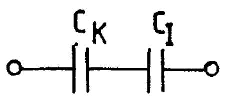


FIGURE 2.23 Equivalent circuit for electrode-dielectric gap.

Since for high-K material, K/K_g may exceed 1000 it follows that h_g/h should be less than 10^{-5} if the effect of the gap is to be negligibl Thus, if h=25µm, h_g needs to be less than 250pm, which is about the diameter of an oxygen ion. Clearly low permittivity layers between electrodes and a thin high-K dielectric must be completely eliminated. Even with plates 0.5mm thick gaps greater than 5 nm are undesirable.

Metals such as silver require to be bonded to a ceramic by a glaze which wets both the silver and the ceramic. Good adhesion must be secured without introducing an appreciable thickness of glaze between the silver and the ceramic. The use of a conductive glaze might help but could lead to a high level of series resistance at high frequencies.

The effect of contact with metal on the behaviour of current carriers in a dielectric has been discussed under 'Absorption currents' in para. 2.4. Whether or not a metal will form a blocking contact depends largely on the surface states that exist at the interface. The work function of most metals exceeds 4eV, which is greater thar the width of the conduction band plus the energy of the highest donor level((2.44) para. 2.4) for many dielectrics so that, in the absence of surface states, the contacts would be blocking. However, there is a layer of oxide on the surfaces of most metals which may provide surface states that effectively lower the work function of the metal below that of the dielectric so that ohmic contacts can be formed. Both nickel-chromium, deposited under vacuum, and nickel-phosphorus, deposited from aqueous solution, give ohmic contacts on barium titanate after annealing at 300 to 600°C. Presumably an interface of nickel oxide is formed during the heat treatment.

Silver usually forms a blocking contact. Since it is most commonly fired or mixed with a glaze and other additives the interface is complex.

Indium, indium-gallium alloys and indium amalgams form ohmic contacts when rubbed on the surfaces of dielectrics.

In most applications the presence of blocking contacts has very little effect on the dielectric behaviour since the voltages applied in use are sufficient to cause electrons to tunnel through the Schottky barriers.

Barrier layers and blocking contacts are of greater importance in very thin vacuum deposited dielectrics in which the Schottky barrier may form an appreciable fraction of the total dielectric thickness. They also affect the behaviour of the thin dielectric layers on the surface of conductive grains in barrier layer capacitors (para. 7.8.2).

2.12 BREAKDOWN

The electrical breakdown of a capacitor is usually catastrophic and design must be such as to make it extremely improbable. Breakdown results in the rapid discharge of the energy in the capacitor and its conversion to heat and mechanical stress. The consequences vary with the type of unit. If it is electrolytic then the effect may be healed by the anodic growth of fresh material. However, more extensive failure may lead to an explosion of the outer container and the widespread distribution of the electrolyte and other contents. The consequences can be tolerable in the case of impregnated paper or polymer film units in which the electrodes are so thin that they are destroyed in the neighbourhood of the breakdown, so isolating the damaged area. The resulting pulse can cause errors in digital logic systems. With thicker electrodes breakdown destroys the capacitor.

The effect of breakdown on a ceramic dielectric is usually to establish a low resistance path between the electrodes due to the migration of metal. If the energy involved is high the unit may be mechanically shattered with a resulting open circuit.

In general inhomogeneities tend to lower breakdown strength so that the greatest strengths are found in glasses, polymers and single crystals. Ceramics need to be free of inclusions and porosity to have strengths comparable to single crystals.

High breakdown strength can contribute to volumetric efficiency if a dielectric can be made thin enough to take full advantage of it. The working voltage, V_w, is relat to the breakdown field, E_b, and the dielectric thickness, h, through a safety factor, η:-

$$V_w = E_b h/\eta \qquad \text{...... (2.73}$$

substituting for h in (6) gives:-

$$C/B = \varepsilon E_b^2/\eta^2 V_w^2 \qquad \text{...... (2.74}$$

(2.74) indicates the advantage of polymer film dielectrics which can be made much thinner than most ceramics and which have high breakdown strengths. Electrolytic units also have very thin dielectrics and, in addition, can operate with lower safety factors. Cerami can be made to form thin dielectris by the 'barrier layer technique which is discussed in detail in Chapter 7. Th excess thickness in conventional ceramic units has the advantage, in some cases, of leading to greater reliabili

Two types of failure are recognised in dielectrics, sometimes distinguished as electrical and electrothermal breakdown. Electrothermal breakdown occurs after a constant potential, or an alternating potential of consta amplitude, has been applied for a time exceeding about 1ms. The term 'thermal' is due to this type of breakdow occurring when high frequency potentials are applied to dielectrics and cause a rise in temperature through dielectric losses. If the rise in temperature at some point in the dielectric is sufficient to cause an increas in dissipation factor, the temperature rise will be accelerated and a catastrophic event may be precipitated. The term has been extended to cover any form of breakdown occurring with a brief delay after the application of a potential. It is distinguished from 'degradation' which may result in breakdown after prolonged periods on test. In the case of degradation the useful life of a capacitor is usually determined by something other than an electric discharge, for instance a fall in capacitance value or resistivity below a specified limit, or an increase in dissipation factor. However, unless the test voltage is removed, degradation usually ends in breakdown. The term 'aging' is applied to an effect found with ferroelectric dielectrics, namely a fall in permittivity and dissipation factor roughly proportional to the logarithm of storage time (see para. 5.1.2.). Aging of this sort does not lead to an increased probability of breakdown.

2.12.1. Electrical Breakdown

Intrinsic dielectric strength is only one of several factors affecting the breakdown voltage of a capacitor. The condition for breakdown is a local field of sufficient magnitude to promote electrons into the conduction band and to impart sufficient energy to them for their impact on other atoms to generate more electrons by ionisation. Thus any flaw or structural feature that leads to a local intensification of an applied field will lower the breakdown strength.

Whilst breakdown strength is measured in units of field, it is not, in practical terms, independent of either the thickness or the area of a dielectric. So far as area is concerned there is an increased probability of including flaws as the area is increased. The fall in strength with increased thickness can, at least in part, be attributed to the field near to certain types of flaw, e.g. thin metallic protuberances from the electrode into the dielectric, being related to the applied voltage rather than to the average field as given by the quotient of the voltage and the dielectric thickness.

The thickness effect is usually expressed by the relation:-

$$E_{bh} = \kappa h^{-y} \quad Vm^{-1} \quad \ldots\ldots (2.75)$$

where κ is a constant (sometimes termed Baur's constant) and y an exponent with a value in the range 0.3 to 0.4 (25,26).

The area effect can be represented by a log-linear equation such as (27):-

$$E_{bA} = \gamma - \Sigma \log A \quad Vm^{-1} \quad \ldots\ldots (2.76)$$

where γ is the breakdown strength for unit area and Σ a constant that usually lies in the 1 to 10 MVm^{-1} range for ceramics. If κ in (2.75) is determined for unit area, the combined effect of area and thickness is given by:-

$$E_b = \kappa' h^{-y}(1-\Sigma'\log A) \qquad Vm^{-1} \quad \ldots\ldots \quad (2.77)$$

where $\kappa' = \kappa/\gamma$ and $\Sigma, = \Sigma/\gamma$.

The most common structural feature limiting breakdown strength is the edge of the electrode. Figure 2.24a shows the crowding of the lines of force that occurs at the edge of an electrode due to the fringing field in the dielectric. The maximum value of the corresponding field is proportional to the square root of the electrode separation.

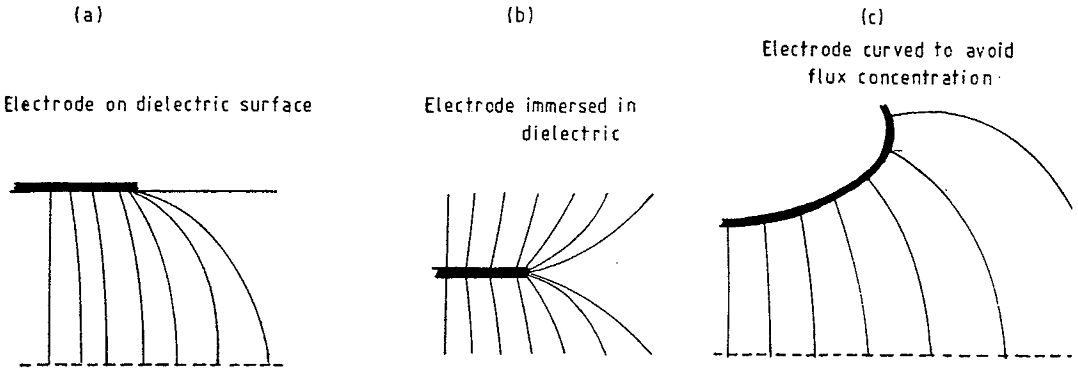

(a)
Electrode on dielectric surface
(b)
Electrode immersed in dielectric
(c)
Electrode curved to avoid flux concentration

FIGURE 2.24 Flux lines at electrode edges.

The field at the electrode edge may be enhanced in multi-layer structures by the overlap of neighbouring electrodes (figure 2.24b). It is largely eliminated in ceramic R.F. power capacitors by thickening the edges of the dielectric so as to spread the lines of force over a larger area of electrode (figure 2.24c)(see also figure 4.13, para. 4.2.5.3.).

Another possibility with high-K dielectrics is to bring the electrodes right up to the edge of the ceramic plate and to coat the bare dielectric between the electrodes with a low permittivity and closely adherent insulating material (158). The fringing effect is greatly reduced, since the lines of force are concentrated in the high-K body, but it is essential that the area between the electrodes is covered by solid insulating material because surface breakdown occurs readily across high-K bodies in air. In the case of ceramic R.F. power units the insulation is usually provided by a layer of glaze covering the electrode edges. In small high voltage units an adherent polymer can be used.

Any sort of cavity in a dielectric may lower the breakdown voltage. A crack in the surface may admit metal from the electrode and provide a protruding spike that will have a high field at its tip. A pore may reduce the effective thickness through breakdown across its surface (28). Conductive impurities have a similar effect. High-K dielectrics may contain low-K phases that lead to local field enhancement as discussed in para. 5.1.7.

All potential causes of breakdown are likely to lead to degradation, and therefore to some form of failure after prolonged use. A voltage breakdown test at a level several times that of the working voltage is therefore of some value in weeding out unreliable units.

2.12.2 Electrothermal Breakdown.

Electrothermal breakdown is largely governed by the temperature and frequency dependence of the dissipation factor combined with the heat conductivity and geometry of the dielectric and will be discussed in the section on power capacitors. It may also occur as the result of some forms of degradation as discussed below.

2.13 DEGRADATION

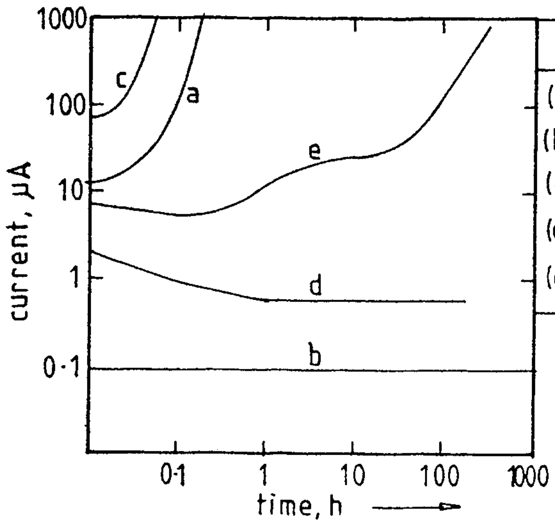
Degradation occurs more frequently in high-K dielectrics but can occur to varying extents in all ceramics. It consists of a more or less sudden fall in resistivity following the prolonged application of a DC field. One form can occur at room temperature with fields as low as 0.03 MVm^{-1} and is particularly noticeable where dielectrics below 50μm in thickness are exposed to high humidities. The other form occurs when the temperature exceeds 80°C and the field exceeds 1 MVm^{-1} (at higher temperatures lower fields may produce the effect).

Low field degradation appears to be due to moisture penetrating into cracks in the ceramic and dissolving ionic impurities such as sodium chloride or barium hydroxide. Silver, derived from the electrodes, may be deposited as fine filaments by electrolytic action and form low resistance paths when they bridge the electrodes. Such filaments are sometimes destroyed by high currents, mechanical vibrations or by the application of higher voltages so that the resulting faults are intermittent.

Encapsulation in polymers can afford some measure of protection against the ingress of moisture, but is less effective at very high humidities at temperatures above 25°C. Glazes have greater impermeability than polymers but in order to prevent the development of cracks, require close matching in thermal expansion to both the dielectric and the metal of the terminations and leads.

The rate of degradation is greatly increased by flaws in the structure of a capacitor and this becomes increasingly apparent as the dielectric is made thinner. The flaws are difficult to detect non-destructively so that care in manufacture is the principal means of ensuring a satisfactory life in use.

The high field form of degradation occurs in many dielectrics containing MO_6 octahedra. A set of current/time relations for ceramic barium titanate is shown in figure 2.25 (29).



	Dopant	Treatment
(a)	none	none
(b)	0·13cation% UO_3	none
(c)	none	wet air, 1000°C
(d)	0·13cation% UO_3	wet air, 1000°C
(e)	none	dry air, 1000°C

FIGURE 2.25 Current v time. Commercial grade $BaTiO_3$ under a field of 0.4 MVm^{-1} at 175°C (29)

From this it can be seen that treatment in moisture containing atmospheres hastens the onset of degradation whilst an additive, in this case uranium oxide counteracts the effect.

This type of deterioration occurs in single crystals as well as in ceramics and has been studied in crystals of rutile. In rutile it is most marked when the c-axis is perpendicular to the planes of the electrodes and is enhanced by heating specimens in oxygen containing water vapour at 850°C. In this case the hydrogen concentration, estimated from the infrared absorption caused by hydroxyl groups, is 6 to 7 ppm relative to the titanium content, compared with 1 ppm for a specimen heated in dry oxygen (30).

The take-up of hydrogen from a moist atmosphere and its passage through a single crystal under the influence of a field has been observed in the case of barium sodium niobate ($Ba_2NaNb_5O_{15}$), a material with a tungsten bronze structure which is based on corner sharing NbO_6 groups. In this case the effect of the hydrogen is to increase the resistivity by three orders of magnitude and to facilitate domain wall movement so that the crystal becomes single domain (31).

The incorporation of protons in a crystal lattice may be through a surface reaction between water, oxygen ions and vacant anion sites (V_O), as:-

$$H_2O + O^{2-}(1) + V_O(1) = 2(OH)^-(1)$$

where (1) signifies location in the crystal lattice. The protons then move through the anion lattice under a field and are discharged at the cathode, with the release of water, by the reverse reaction. Gold anodes have been found to inhibit degradation in barium titanate (29) ceramics which suggests that more complex reactions involving catalytic action by the electrodes may be involved.

The increase in resistivity in barium sodium niobate may be due to the neutralisation of uncompensated charged vacancies that inhibit domain wall movement. It is notable that the initial effect in rutile is also an increase in resistivity (30).

Degradation has not been reported for single crystal barium titanate or for the hot-pressed ceramic. It can be inhibited in air sintered ceramics by annealing them i bismuth oxide vapour so that the intergranular region tak up bismuth. Grain boundaries, where there are a high concentration of defects, are evidently of primary importance in this case (32). On the other hand it has been found that changes in grain boundary area due to changes in grain size in the range 1 to 10µm do not affect degradation, whilst the presence of pores accelerates its onset (33). This suggests that the presence of internal interfaces between solid and gas phases is of importance. The increase in dissipation factor resulting from porosit (para. 2.3.1.) is evidence of the presence of structures with low energies of activation in internal surfaces. Pores are also capable of acting as both sources and sink for the oxygen vacancies which play an important part in the process of degradation. It is probable that the effect of grain boundaries varies between different preparations since it depends on the morphology and composition of the secondary phases contained in them.

On applying a field at a temperature above 200°C to a air sintered barium titanate ceramic, a low resistivity region first develops at the cathode accompanied by a blu colouration with a white edge on the side away from the electrode. At the same time a brown colouration develop at the anode with a pale zone adjacent to the electrode. Both coloured areas increase with time and the blue regio eventually penetrates through the brown and reaches the clear zone. At low fields this condition may be stable but at higher fields blue spikes penetrate through to the anode and the resistivity falls to a low level (32).

In single crystal rutile highly conductive filaments develop along the c-axis (34) when a field is applied in that direction. There is no similar development when th field is applied in a perpendicular direction. Degradation is slower in ceramic rutile which may be due to the random orientation of the grains. However, the development of conductivity in one grain results in an increase in the field acting on neighbouring grains. Moreover, there will be flux crowding at the tip of a filament which will result in high local fields, so that conductiv paths may spread through a ceramic by a similar mechanism to that in a single crystal.

The onset of degradation can be considerably delayed by the substitution of the ions of the main phase by ions of higher positive charge, e.g. Nb^{5+} for Ti^{4+}, Bi^{3+} for Ba^{2+} and F^{-} for O^{2-}. The resulting excess positive charge reduces the concentration of oxygen vacancies and hydroxyl groups and therefore the total concentration of mobile defects. As these defects have positive charges they accumulate at the cathode and, as they behave as donors, they result in a local low resistivity region.

Additions of small amounts of manganese improve the properties of a wide range of medium- and high-K dielectrics by reducing their dissipation factors and by inhibiting degradation. Manganese, in air fired bodies, is present as Mn^{4+} and Mn^{3+} on B-sites and counteracts the formation of Ti^{3+} ions caused by the presence of an excess of oxygen vacancies. The conversion of Mn^{4+} to Mn^{3+} occurs more readily than other similar charge changes in transition elements. The function of manganese as an acceptor impurity is discussed in para. 6.3.2.3.

It is found that in rutile the presence of manganese increases the formation of hydroxyl groups that results from heating in moist air, in contrast to the effect of niobium substitution which largely suppresses the uptake of hydrogen. The concentration of Mn^{4+} is found to increase at the anode and decrease at the cathode when a field is applied at a high temperature, which is the result to be expected if the change in concentration of oxygen vacancies is being compensated by a change in the manganese ion charge (30).

Manganese can also function as an oxygen conductor through its oscillation in valency. It may therefore facilitate the movement of oxygen from grain boundaries into the grains while a ceramic is cooling after sintering and so eliminate some of the oxygen vacancies formed at high temperature that would otherwise be frozen in.

The deterioration in the resistivity of a dielectric can usually be reversed simply by removing the applied field for a prolonged period or, more rapidly, by simultaneously raising the temperature a few hundred degrees. The entities displaced by the field evidently diffuse back to their equilibrium sites and restore the dielectric to its initial state.

Whilst a satisfactory mechanism for the degradation process has yet to be suggested, the following steps can be taken to minimise its effect:-

1. Add Nb, Ta, U or Mn as B-site substituents or Bi to replace some of the A-site ions.
2. Anneal in dry air, preferably in the presence of a source of fluorine (see also para. 5.2.6).
3. Encapsulate in a medium, preferably a siliceous glaze, with a minimum permeability to water vapour.
4. Hot-press, or densify by an anneal at high temperature under pressure after sintering.
5. Use gold for the electrodes.

Currently only step 1 is taken. The others have been shown to be effective but add significantly to the cost. However annealing under pressure has been shown to heal flaws in the structure of multilayer capapcitors and may be acceptable for small units (see para. 3.3.3).

High-K dielectrics containing lead oxide, which are coming increasingly into use, suffer from this problem to a lesser degree than those containing alkaline earth ions.

Some other effects of hydroxyl groups on barium titanate dielectrics are described in para. 5.2.6.

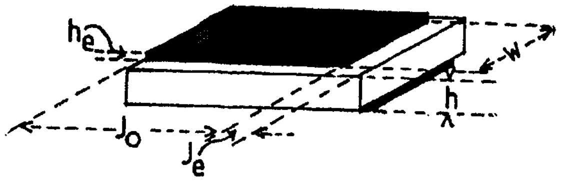
6

Monolithic Multilayer Capacitors

Volumetric efficienty demands thin dielectrics but large areas of thin dielectric are fragile. One attempt to solve this problem has been to extrude thin walled tub and, after electroding, to glue them together as raft shaped units, but this is too expensive. A more success ful solution is the multilayer structure, with the result ing units, when unencapsulated and without leads, often termed chips since they are roughly cubic with edge lengths of a few millimetres. The dielectrics may be NP or high-K. To date most of them contain substantial pro portions of Ti^{4+} ions though compositions containing Nb^{5+} ions in their place are being introduced. Methods of manufacture have been discussed in paras. 3.2.5 to 3.2.9.

6.1. ELECTRODE METALS

The structure, a stack of thin ceramic plates co-fire with interleaved electrodes, figure 6.1, has been outline and some aspects discussed in para. 2.9. If the units a fired in air the dielectric properties are very close to those of single plate units with silver electrodes applie after sintering. However, air firing leads to limitatio in the metals that can be used for the electrodes. Platinum, platinum-gold alloys and gold can be used to cover the temperature range 800-1500°C with most dielectrics when sintered in air, but are expensive. Palladium can be used in contact with barium titanate up to 1500°C but its melting point is reduced in contact with ceramics containing lead or bismuth oxides.



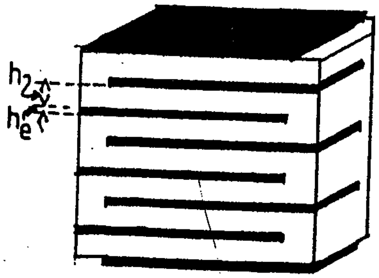


FIGURE 6.1 Dimensions of monolithic stack.

Palladium and silver form solid solutions with melting points approximately proportional to the content of the end members, silver m.p.960 and palladium m.p.1550°C, and these can be used at sintering temperatures below 1300°C. The interaction of electrodes and ceramic diminish as the sintering temperature is reduced so that ceramics containing high proportions of lead oxide can be co-fired with silver-palladium alloys below 1200°C. Theoretically silver could be used on its own below 960°C but the facility with which it migrates through ceramic structures can lead to low resistance failure with thin dielectrics at high fields, particularly in the presence of traces of moisture or at high temperatures. Alloying with 10-15% palladium reduces the migratory tendency whilst an addition of gold diminishes it still further (69).

If the units are fired under reducing conditions, oxygen pressures of 1 to 10^{-6}Pa, so that base metals can be used as electrodes, suitable acceptor ions must be added to barium titanate to prevent the dielectric becoming conductive. This results in some limitation to the high-K compositions that can be used, whilst the firing of the accepted NPO compositions at low oxygen pressures has not been sufficiently investigated. Even with acceptor doping it is to be expected that the dissipation factors of titania containing dielectrics will be increased though their resistivities may be adequate. Dielectrics based on less reducible oxides, such as zirconia, can be sintered without dopants at low oxygen pressures to give low loss dielectrics with controlled TCCs, but with lower dielectric constants (13-40) than those based on titanates (187).

Lead and bismuth must be omitted from dielectrics intended to be sintered in reducing atmospheres.

Conductive oxides can be used as electrodes that can l fired in air in contact with barium or lead based dielectrics. The very high reactivity of oxides when in conta(with one another at high temperatures limits the possible combinations of conductive and dielectric oxides but, at the same time ensures that intimate contact is obtained between the two phases (220).

A fourth method of electroding consists in depositing fugitive material in the region where the electrodes are required so that on burning out and sintering vacant gaps connected to the outer surface are formed between the dielectric layers. These gaps can then be filled with metal by immersing the units under liquid metal and applying first a vacuum and then pressure.

This method is applicable to all the established air fired compositions. The electrode thickness has to be somewhat greater than that used with co-fired electrodes, which may result in a small reduction in volumetric efficiency.

6.2. DIMENSIONAL CONSIDERATIONS

The electrodes must be sufficiently thick to avoid th(introduction of a series resistance that will seriously increase the dissipation factor of the capacitor (see par: 2.11). An approximate expression for the dissipation factor introduced in this way is given by (2.70) para. 2:10:-

$$d_s = 4\pi\nu C(\rho_e/h_e)(J_o/w) \qquad \ldots\ldots \quad (2.70)$$

The dissipation factor can be reduced by having a low length to width ratio and by having thicker and more conductive electrodes. 3μm thick palladium electrodes intr(duce a dissipation factor of 0.02 in a 48nF capacitor at 1MHz (impedance 3.3Ω) so that electrode thicknesses of th: order of magnitude are adequate with high-K dielectrics ı most applications.

In NPO units the tolerable increase in dissipation factor due to the electrodes needs to be kept below 10^{-3}, giving a capacitance limit of 2.4nF for 3μm palladium electrodes. Since the electrode structure is such that the resistivity exceeds that of the fully dense metal by a small factor, some consideration needs to be given to the electrode thickness where relatively high value low loss units are intended for high frequency applications.

Equation (2.60)(para. 2.10) gives an estimate of the inductance of a capacitor stack. Combining this with (2.58) and putting J=w (which gives minimum inductance) an approximate expression for the self-resonant frequency, ν_r, of a chip capacitor is:-

$$\nu_r \simeq 240(JC)^{-\frac{1}{2}} \quad \text{Hz} \quad \ldots\ldots \quad (6.1)$$

The self-resonant frequency is not affected by the number of plates because each plate between two electrodes has the inductance of N units in series with it whilst the whole stack has the inductance of N times that of each two electrode units. It follows that a multilayer stack should have a higher self-resonant frequency than the same dielectric made into a single plate capacitor with the same capacitance.

It would appear from these considerations that stacks should be roughly cubic in shape. How far this is carried depends on the technical problems involved: for instance there are possible difficulties in forming stacks of less than 2mm edge dimensions. Also the margins necessary to allow for variations in registration, possibly 0.5mm, begin to take up an appreciable fraction of the available dielectric in units of small sectional area.

The cost of the elctrodes is proportional to their thickness and area.. The mass, M_e, not allowing for non-overlapping areas, is given by:-

$$M_e = D_e(C/\varepsilon)h_d h_e \quad \text{Mg} \quad \ldots\ldots \quad (6.2)$$

where h_d and h_e are the dielectric and electrode thicknesses, and D_e the density of the electrode metal. Taking h_d=25x10^{-6}m, h_e=3x10^{-6}m, K=5000, C=1μF, D_e=11Mgm^{-3}, M_e, according to (6.2) is 0.02g. Clearly if the electrode metal costs 200 cents per gram it adds significantly to the cost of high-K units in the microfarad range.

6.3. MANUFACTURING METHODS

The general principles of bandcasting, electroding, stacking etc. have been outlined in para. 3.2.6. and appl to all three types of unit. There are variations in the methods of stacking. Individual plates may be stamped from the electroded green film and stacked under pressure or pieces with an array of electrode patterns on them may be stacked and pressed to form pads from which individual units may be stamped or cut. The latter method applies particularly to the smaller units but has the disadvantag that stamping out the units may distort the dielectric layers and cause delamination (but see para. 3.2.6.).

6.3.1. Precious Metal Electrodes

Precious metal electrodes permit sintering in air and therefore allow the use of a wide range of dielectric compositions.

The paint used for silk-screening contains the metal particles 1μm or less in diameter. No additives are usually necessary in order to secure adhesion and both platinum and palladium sinter satisfactorily with barium titanate in the 1200-1450°C temperature range. However, as pointed out in para. 2.8, extremely close adhesion between electrodes and dielectric is essential, especiall when the dielectric is thin, and some of the variability capacitance that occurs may stem from gaps only a few hundred picometres wide.

The electrode layers emerging at the sides of the sta are most commonly interconnected by applying silver paste after sintering and refiring at 600 to 800°C. In this case the usual addition of a glaze ensures good adhesion.

Platinum and palladium have a small solubility in barium titanate at high temperatures and this may assist the formation of close contacts between the two phases. No deleterious effects have been reported. Silver is soluble in compositions having a high lead content and, i at least one case, has a distinct effect on the dielectri properties, but is not particularly disadvantageous (see para. 5.3.2.).

A combination of silver electrodes with one of the compositions discussed in para. 5.3.2 and 5.3.3. that sinter at low temperatures, provides the most economical raw materials for multilayer stacks. However, about 15% palladium must be retained in order to restrict the tendency of silver to migrate along grain boundaries.

The sintering temperature of barium titanate can be lowered to 1100°C by providing a liquid phase (see para. 3.3) based on a eutectic formed between CuO, Cu_2O and $BaTiO_3$ that melts at 1070°C, provided that the ambient oxygen pressure exceeds $0.4x10^5$Pa. The high oxygen pressure is necessary to prevent the complete dissociation of CuO to Cu_2O. However, an addition of TiO_2, GeO_2 or Al_2O_3 lowers the melting point to 1000°C which allows sufficient CuO to be retained in air.

When 0.25 to 0.5 cation% of cupric oxide and a similar quantity of, for instance, germanium oxide is added to calcined barium titanate the mixture sinters satisfactorily at 1020°C but the temperature is finally raised to 1100°C. The eutectic composition is found to segregate at the triple junctions between the grains, possibly because the dissociation of the cupric oxide at the higher temperature alters the wetting properties of the liquid immediately before it solidifies.

The method can be applied to a wide range of titanate composition, including NPO types, and allows the use of a 30/70 Pd/Ag alloy for the electrodes (65).

6.3.2. Base metal electrodes

The equilibrium oxygen pressures for a selection of oxides as calculated from their free energies are shown in figure 6.2. Nickel, cobalt and iron and their alloys form suitable electrode materials because they remain in the metallic state in atmospheres that contain sufficient oxygen to allow suitably doped ceramics to form high resistivity dielectrics. Nickel, m.p.1452°C, is the most satisfactory choice since it withstands the presence of oxygen at higher pressures than iron and is considerably more abundant than cobalt.

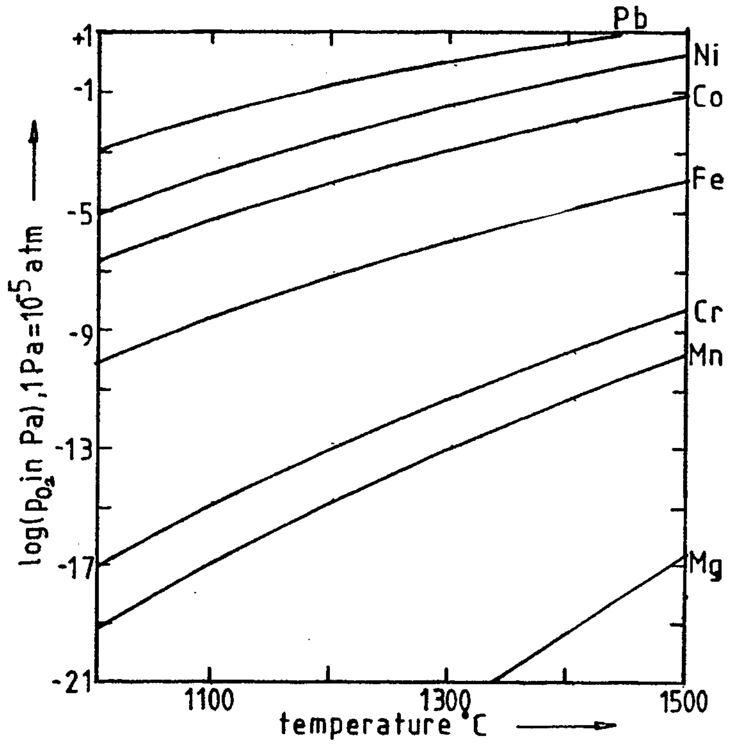


FIGURE 6.2 Equilibrium oxygen pressures for metal/metal oxide systems

6.3.2.1. Controlled atmospheres

Close control of oxygen pressure is obtainable by mixing carbon monoxide and dioxide or by mixing hydrogen and water vapour. The oxygen pressure calculated from t equilibrium constants of the reactions:-

$$CO_2 \rightleftharpoons CO + \tfrac{1}{2}O_2$$

$$H_2O \rightleftharpoons H_2 + \tfrac{1}{2}O_2$$

are shown as functions of temperature in figures 6.3 and 6.4. As these relations are approximately parallel to t dissociation pressure-temperature relations for the oxide a constant gas composition can be maintained throughout t sintering cycle (188).

Hydrogen-water atmospheres are conveniently obtained mixing a 10% hydrogen in nitrogen gas with air.

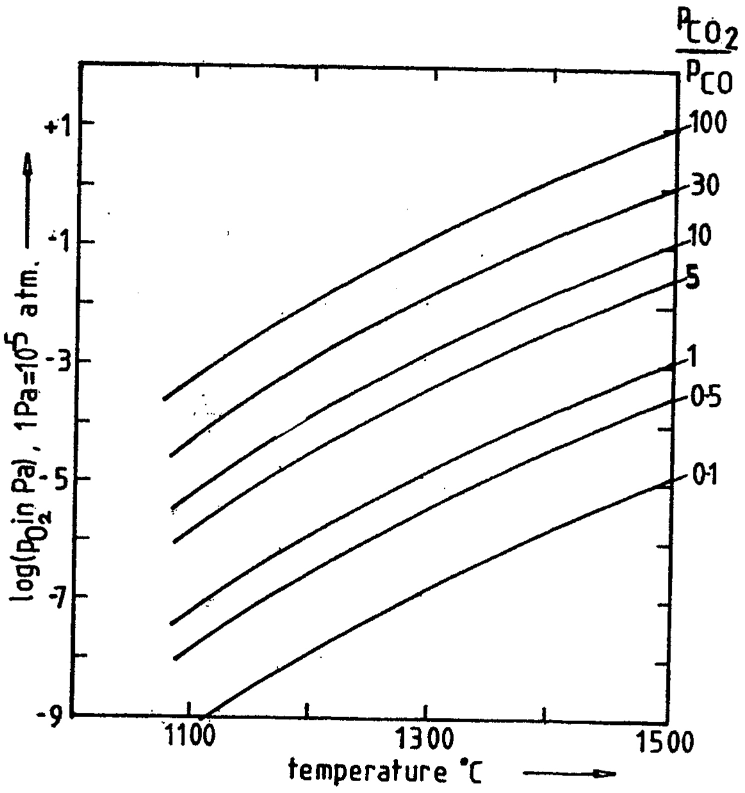

P_{CO_2}
P_{CO}
100
30
10
5
1
0·5
0·1
+1
-1
-3
-5
-7
-9
log(p_{O_2} in Pa), 1Pa=10^{-5} atm.
1100
1300
1500
temperature °C

FIGURE 6.3 Oxygen pressure v temperature and composition for $CO+CO_2$

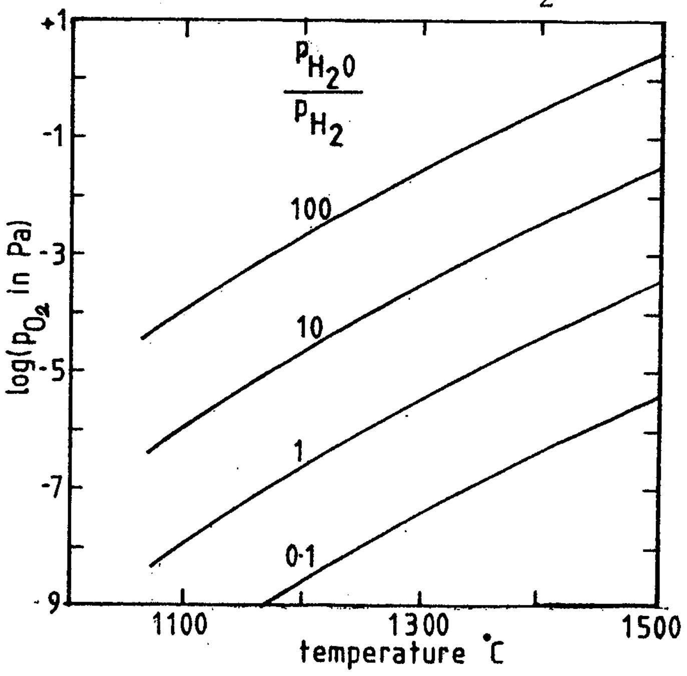

P_{H_2O}
P_{H_2}
100
10
1
0·1
+1
-1
-3
-5
-7
-9
log(p_{O_2} in Pa)
1100
1300
1500
temperature °C

FIGURE 6.4 Oxygen pressure v temperature and composition for H_2O+H_2.

Sintering with base metal electrodes has also been carried out in 'oxygen free' nitrogen (189) but unless this is combined with the use of an oxygen sensor, such a a zirconia cell, the oxygen pressure is ill defined and leaks from the atmosphere may cause oxidation of the electrodes.

6.3.2.2. Dopants

The prevention of the development of conductivity through sintering in a reducing atmosphere depends on the inhibition of the formation of Ti^{3+} ions and the neutrali tion of the effects of the oxygen vacancies which compensate for the reduction in cation charge. Ti^{3+} formation can be prevented by providing a more readily reducible io on the B-site, e.g. Mn^{3+}, Co^{4+} or Fe^{3+}, or by the substiti tion of titanium by a lower valency ion such as Mg^{2+} or Ca^{2+}. In the latter case the presence of an excess of A-site ions is necessary (see para. 5.2.1.2.).

These substitutions do not inhibit the formation of oxygen vacancies but inhibit their effect, as shallow electron traps providing current carriers at room temperature, in two ways. Firstly by the formation of stable anion vacancy-B-site defect pairs (190) and, secondly, by the acceptor properties of isolated B-site defects. Holes formed in the valency band due to the presence of acceptors do not contribute significantly to the conductivity because of their low mobility (191) but they can be replaced by electrons from donors.

The choice of variable valency ions is, to some exter limited by the possibility of their reduction to the metal lic state in a separate phase. Figure 6.2 gives an indication of the readiness with which this may occur, though the dissociation of the oxides is influenced to varying extents by the modification to the activities of the ions resulting from their being in solid solution in barium titanate. It is, however, evident that the oxyger atmosphere can be adjusted so that cobalt, iron, chromium and manganese will remain as ions in the ceramic while nickel remains in the metallic state during sintering. It can also be seen that cobalt and iron could be used as electrodes under an oxygen pressure that would allow manganese to be retained as a divalent ion, and chromium in the trivalent state.

It has been found that the protective effects of dopants on a barium titanate ceramic, containing 6.8 cation% Ca and 6.8 cation% Zr, decreases in the order Mn, Co, Mg, Cr, Ga, Fe (188). A calculation based on the ability of a dopant ion to trap an electron by reducing its positive charge gives the order of effectiveness as Zn^{2+}, Ni^{3+}, Cu^{2+}, Mn^{3+}, Co^{3+}, Cr^{3+}, Fe^{3+}, V^{3+}. Ga^{3+}, Ti^{3+} (192) which compares well with the experimentally determined order when the ready reduction of zinc, nickel and copper to the metallic state is taken into account.

6.3.2.3. Manganese.

Mn_2O_3 forms a solid solution with the hexagonal form of $BaTiO_3$ up to the level Mn_2O_3, $BaTiO_3$ (193). The calcination of mixtures of $BaCO_3$, TiO_2 and $MnCO_3$ at 1100°C in air leads to the formation of a mixture of tetragonal and hexagonal phases when the manganese content exceeds 5 cation%. At lower concentrations Mn^{4+} is present in a cubic phase with a diffuse X-ray diagram.

The presence of Mn^{2+}, Mn^{3+} and Mn^{4+} in $BaTiO_3$ ceramics, containing up to 1 cation% Mn and fired in air in the 1300-1400°C range, can be inferred from electron spin resonance observations (194).

When manganese carbonate is added to calcined barium titanate, prior to sintering in air, grain growth is inhibited up to 1350°C and little of the manganese passes into the main phase. Grain growth occurs at 1400°C and is accompanied by a take up of some 50% of the available manganese (195).

In reducing atmospheres manganese tends towards the divalent state and a separate MnO phase appears. Some Mn^{2+} remains in the $BaTiO_3$ lattice, probably on the B-site, except, possibly, at very high temperatures and very low oxygen pressures (197). The ionic radius of Mn^{2+} in the low spin state is 0.67pm, in the more usual high spin state it is 0.82pm. It may therefore have a solubility similar to that of Mg^{2+}, radius 0.72pm, i.e. slight, except in the presence of excess BaO, the AO/BO_2 ratio does not affect the properties of manganese doped barium titanate dielectrics to any marked extent.

Manganese reduces the Curie point of barium titanate only a small extent when sintered or annealed in air at temperatures above 1000^oC but it is lowered appreciably when doped compositions are annealed at low oxygen pressures. The reduction reaches a maximum of -80^oC/cation% for an oxygen pressure of 10^{-7}Pa (195) which is close to that to be expected from the creation of oxygen vacancies in undoped barium titanate. There is, therefore a marke change in Curie point when air fired manganese preparatio are annealed in reducing atmospheres.

In practice a manganese compound is usually calcined air with barium carbonate and titanium dioxide so as to form a solid solution before sintering. The sintering atmosphere is either oxygen free nitrogen, a CO/CO_2 mixtu with a CO content around 10% or a mixture of nitrogen, hydrogen and water vapour formed by mixing 10% H_2 in N_2 with air. The highest room temperature resistivities ar obtained with manganese contents below 1 cation% and oxyg pressures of about 0.01 Pa. Nickel oxidises and dissolv in barium titanate at 1350^oC under an oxygen pressure of 0.1 Pa or more.

Manganese doped dielectrics sintered under reducing conditions show a deterioration in resistivity, typical o dielectrics containing a high concentration of oxygen vacancies, when exposed to high DC voltages at temperatur above 100^oC, as illustrated in figure 6.5. This degradation is lessened by annealing in a higher oxygen pressure than was used for sintering (188).

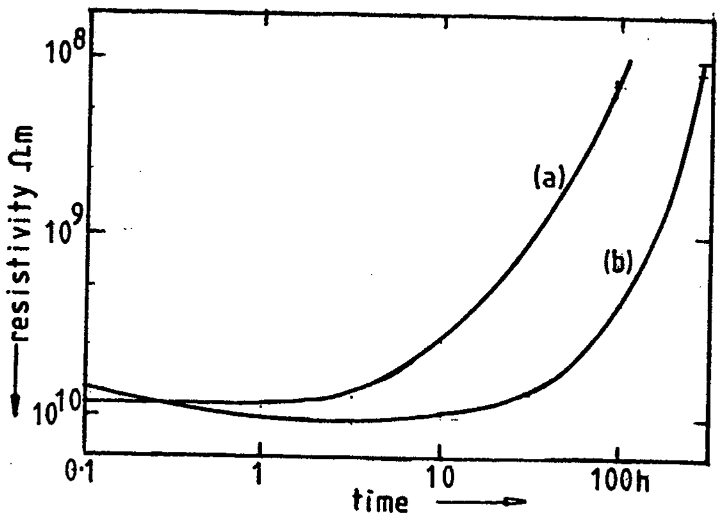


FIGURE 6.5 Resistivity v time at 125^oC under a $2MVm^{-1}$ DC field for Mn doped $BaTiO_3$ sintered at 1350^oC in (a) 10^{-3} (b) 10^{-5} Pa O_2. Both annealed 2h at 1300^oC in 10^{-2}Pa O_2. (188)

6.3.2.4 Other dopants

The correlation between degradation and a high oxygen vacancy concentration makes it desirable to minimise the latter by reducing the concentration of acceptors. The use of trivalent instead of divalent ions may also be advantageous since this halves the number of accompanying oxygen vacancies. Chromium which gives Cr^{4+} ions under oxidising conditions and Cr^{3+} under reducing conditions may therefore be preferable to manganese which yields Mn^{4+} and Mn^{2+} under the same conditions (65).

Nickel has a protective action similar to that of cobalt and it has been suggested that it can be introduced by sintering a multilayer stack in an atmosphere allowing the slow formation of nickel oxide (196). The oxygen pressure is maintained in the range 0.018 to 0.15 Pa during sintering at 1370^oC for 2½ h using about 25 vol. CO_2 to 1 vol.CO. Both high-K and NPO dielectrics that are normally air fired can be prepared in this way though there is a significant reduction in leakage constant compared with air-firing. Good contact appears to be maintained between the electrodes and the dielectric.

Magnesium has a protective action and has been used with barium titanate and nickel electrodes in a nitrogen atmoshpere (197). Rather high levels of magnesium, 2.5 tc 27 cation%, combined with high AO/BO_2 ratios, appear to give the best results. The resistivity of the resulting dielectrics falls off under DC stress at high temperatures.

Calcium protects against reduction provided that the AO/BO_2 ratio ($A=CaO+BaO$, $B=TiO_2+ZrO_2$) lies in the range 1.005 to 1.03 and oxygen pressure lies in the range 0.1 to 1 Pa. A typical composition contains Ba 42.7, Ca 7.54, Ti 42.3, Zr 7.46 cation% and gives a peak dielectric constant of 10,000 with a fall of 50% at -30 and +85^{o}C. The leakage constant is 5,000s at room temperature (138). It is evident that at the sintering temperature, $\simeq$1330^{o}C, the oxygen pressure is in the range that causes solution of nickel in the dielectric which assists in the protection against reduction. However, the properties have been measured using single discs of dielectric with In-Ga electrodes applied at room temperature after sintering. The leakage constant is then over 1000s so that calcium substitution is the major factor countering the effect of the reducing atmosphere (see also para. 5.2.1).

Multilayer stacks based on this type of composition do not show degradation at 85^{o}C under DC bias and are also satisfactory at 85^{o}C 85% relative humidity at 1.5V DC bias (198).

6.3.3. Injected Electrodes

One of the advantages of the injected electrode proces: is that any dielectric may be used, whether fired in air o1 any other atmosphere. The only condition is the establishment of highly porous layers where the electrodes are to be formed. This is achieved by printing the electrode patterns with an ink containing carbon or organic particle: mixed with ceramic particles of the same composition as th(dielectric. The ceramic constituent has a particle size close to that of the thickness of the final cavity since the particles are intended to form pillars preventing the two major surfaces of the cavity from coming together.

The required cavity is formed by burning out the carboı and organic material and the stack is then sintered. After firing, the sides of the stack where the cavities reach the surface are coated with a silver paint which is fired on at 400-600°C (199). The capacitors are next subjected to reduced pressure and immersed in liquid lead. Pressure is then applied to force the lead into the cavities after which the units are lifted from the lead bath and shaken free of surplus metal. It is probably necessary to add silver to the lead in order to prevent the interconnecting silver from dissolving. There may also be some advantage in having the injected lead wet the ceramic which might be accomplished by first depositing silver in the cavities by filling them with molten silver nitrate (M.P.212°C) and pyrolysing the nitrate at 700 to 800°C (200) to form an adherent deposit of metallic silver.

The electrodes are thicker than those printed directly onto the unfired dielectric by a factor of about 5. Whilst this reduces the volumetric efficiency it ensures the formation of sound connections between the plates, which is often difficult with the thinner, directly formed, electrodes, so that the series resistance due to the electrodes and their interconnections is lower. The presence of the ceramic pillars in the electrode cavities also reduces the volumetric efficiency somewhat.

The process has been established commercially and has proved competitive with the alternative methods. As it can be applied over the whole range of established ceramic dielectrics there is no difficulty in obtaining a suitable combination of dielectric properties and reliability based on prior experience with single layer units.

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